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COMPLEX IONS  
IN AQUEOUS SOLUTIONS



# COMPLEX IONS

IN AQUEOUS SOLUTIONS

BY

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## PREFACE

IN compiling this volume the needs—and criticism—of a large class of students unversed in physical chemistry have been especially kept in view, and it is considered that the introduction of some elementary matter, such as proofs of formulæ, which the advanced reader will not require, is by no means out of place.

In giving an account of the methods in Chapters III.–VI., it was found necessary to introduce examples, but these were made as brief as possible in order to avoid confusing these chapters with the later ones which deal with practical investigations, where more than one method is generally used at a time. The tension experiments in Chapter VIII. form a method of investigation in which the examination of different salts shows so little variation that it appeared unnecessary to devote a separate chapter to the method.

The chief aim of the book is to give some account of the more important experimental work in this subject, and no apology is offered for the absence of theories of valency.

Chapter X. contains an account of some results besides the identification of complex compounds, which have been arrived at by similar methods, and which are likely to form the basis of further experiments.

A. J.

POLMONT,  
STIRLINGSHIRE.  
*May, 1914.*

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## CHAPTER I

### INTRODUCTION

#### A. Introductory.

The suggestion that the abnormal behaviour of certain electrolytes might be accounted for by assuming the formation of complex ions in them was first put forward by Hittorf, who, in the course of his study of migration, made the classical discovery that the migration ratio for the anion in solutions of many double salts and certain single ones increased rapidly with increase in the concentration of the solution and at high concentrations became greater than unity. Hittorf suggested that this was due to the formation of a "double salt" in the solution, which gradually dissociated on dilution. In this way our knowledge of the mode of ionisation of a number of salts in solution was established.

Later, the subject was investigated by other methods, notably by pure chemical means and by cryoscopic measurements. The latter method, however, yields somewhat uncertain results.

A new method was introduced by Roloff (*Zeit. phys. Chem.*, **13**, 341 (1894)), who measured the distribution ratio of a solute between two solvents, and showed that the increase in the solubility of bromine in water observed on adding potassium bromide to the system is due to the formation of the complex ion  $\text{Br}_3'$ . Two years later Jakowkin (*Zeit. phys. Chem.*, **20**, 19 (1896)), employing the same method, found that solutions of iodine and potassium iodide show similar behaviour.

In the last fifteen years two new methods of investigating



the constitution of electrolytes have been worked out, the first based upon solubility measurements and the second upon measurements of electrode potential, and a large number of complex ions have been discovered and studied by these methods. Much of this work was carried out by the late Professors Abegg and Bodländer and their pupils.

Such investigations are likely to be of value in framing a theory of chemical combination in the future. For in complex ions we have a class of compounds in which valencies other than the normal valencies of the elements entering into them are exercised, and whose dissociation constants can in some cases be measured, so that we can gain some information about the action of these weaker valencies.

An ingenious theory of valency which is specially applicable to the formation of so-called molecular compounds (including complex ions) has been constructed by Abegg and Bodländer (Abegg and Bodländer, *Zeit. anorg. Chem.*, **20**, 471 (1899); Abegg, *Zeit. anorg. Chem.*, **39**, 333 (1904)). According to this theory, the tendency which an element exhibits to form complex compounds depends largely upon its electroaffinity, *i.e.* the free energy with which it takes up an electric charge and becomes converted into an ion. It is assumed that the electrolytic potential is an approximate measure of this quantity, though, as Abegg and Bodländer point out, this would only be true if the concentration of free atoms in saturated solution were the same for all elements. Actually, nothing at all is known of the relative solubilities of the metals in water, and in the case of oxygen and the halogens it is very unlikely that at a given pressure the concentrations of the free atoms in aqueous solutions are equal. It is, however, true that, generally speaking, the less the electrolytic potential (either positive or negative) of an element, the greater is its tendency to enter into complex compounds. The electrolytic potential also shows a certain relationship to the atomic volume, the two quantities being roughly parallel in any given group in the periodic system. In the horizontal rows, the electroaffinity shows a continuous

diminution as we pass from left to right, except in the cases of the first two subsidiary groups, namely, of the three pairs of elements, copper and zinc, silver and cadmium, gold and mercury. In these cases the electroaffinity rises rapidly as we pass from left to right.

Abegg distinguishes two kinds of valency, which he calls "normal" and "contra"-valency respectively. The normal valencies of an element are those which are usually active, while the contra-valencies are those which are only occasionally called into play, as in molecular compounds, and are always of opposite sign to the normal ones. From a consideration of valency in relation to the periodic table, he suggests that the total number of valencies of all elements is eight. Usually less than this number are called into action.

#### **B. Definition of the term "Complex Ion."**

A definition of the term "complex compound" which enables us to study the subject according to a definite system was given by Abegg and Bodländer (*loc. cit.*). According to this definition

*Complex compounds are those in which a part of the compound which forms an ion by electrolytic dissociation consists of a molecular compound of a molecule capable of forming a separate ion with an electrically neutral molecule.*

*By the term "Complex Ion" we understand this molecular compound when it has taken up its natural electric charge.*

A complex ion consists of one or more "separate ions" and a neutral part. This neutral part may, in terms of the theory, contain one or more neutral molecules, but in all the complex compounds that have been studied as yet only one neutral molecule has been found.

For example, potassium ferrocyanide consists of the two ion-forming parts  $4K$  and  $Fe(CN)_6$ . The latter part may be regarded as a molecular compound of the separate ion-forming parts  $4CN$  and the neutral molecule  $Fe(CN)_2$ . It forms

the complex ion  $\text{Fe}(\text{CN})_6'''$ , which is a molecular compound of the separate ions  $\text{CN}'\text{CN}'\text{CN}'\text{CN}'$  and the neutral part  $\text{Fe}(\text{CN})_2$ .

It may be asked whether this definition includes all ions which can be regarded as formed from a known neutral molecule and another ion; for example, is  $\text{SO}_4''$  a complex ion which could conceivably be formed from  $\text{SO}_3$  and an oxygen ion?

Abegg (*loc. cit.*) says Yes; oxy-acids are to be regarded as complex compounds yielding complex anions, which consist of a neutral part (the anhydride of the acid) and one or more oxygen ions. The oxygen ions are attached to the molecule of acid-forming oxide by the positive contra-valencies of the oxygen atom and the negative normal valencies of the element forming the oxide. Thus, such ions may be represented by the formulæ  $\text{SO}_3.\text{O}''$ ,  $\text{Cl}_2\text{O}_7.\text{O}''$ ,  $\text{N}_2\text{O}_5.\text{O}''$ , etc. A similar argument applies to the thio-acids, such as  $\text{H}_3\text{AsS}_3$ , etc. This suggestion is ingenious, but somewhat speculative. We shall, therefore, confine ourselves to the consideration of complex ions in which valencies other than the ordinarily-accepted valencies of the elements concerned are certainly called into action.

*Definition of the term "Molecular Compound."*

In the definition given above of complex compounds and complex ions we have used the term "molecular compound," and for the sake of completeness we may define this as follows:—

*Molecular Compounds are compounds of two or more molecules with one another, or of one or more molecules with one or more atoms or ions, in which the molecules, atoms, or ions are held in combination with one another by valencies which were not in action in the single components before combination.*

From this definition it follows that all double salts are to be classed as molecular compounds. Most of these yield complex ions in solution, but in very varying quantities, i.e. the complex ions are of various degrees of stability.

Thus, we can have an indefinitely long series of salts lying between the stages where complex-formation and dissociation respectively are complete. Extreme examples are potassium ferrocyanide on the one hand, where the dissociation of the  $\text{Fe}(\text{CN})_6'''$  ion is so small that no ferro-ion is recognisable in its solutions by chemical means; and, on the other hand, the alums, in dilute solutions of which at most only minimal quantities of complex ions exist (see Abegg and Bodländer, *loc. cit.*). The tests for small amounts of complex ions are, however, by no means delicate, and even in the case of double salts where no complex-formation is recognizable, it seems highly probable that the difference from salts forming more stable complexes lies only in the intensities of the affinities concerned.

On the other hand, some complex ions are formed in solution which do not correspond to any known solid salt.

## CHAPTER II

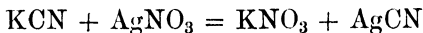
### THE CHEMICAL METHOD

PRACTICALLY all metallic salts become ionised on solution in water, and all reactions between them are reactions between ions. With the exception of cases where a stable complex is formed or a very insoluble compound precipitated the ions present in recognisable quantities in a solution obtained by mixing two electrolytes are those contributed by the two single electrolytes, subject to comparatively small alterations in concentration due to differences in the strengths of the original solutions and reactions tending to produce more or less of the undissociated salts. (The last case may be held to include the precipitation of a salt which is not very insoluble, with respect to which the solution may become supersaturated.) Thus, if we mix solutions of silver nitrate and potassium sulphate all the four ions will be recognisable in the resulting solution. If the original solutions were strong some silver sulphate may be precipitated, but on filtering this off the solution will be found to contain the ions  $\text{Ag}^+$ ,  $\text{NO}_3^-$ ,  $\text{K}^+$ , and  $\text{SO}_4^{2-}$ .

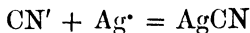
Suppose that instead of using potassium sulphate we add potassium cyanide to a solution of silver nitrate in small quantities at a time. At first silver cyanide is precipitated. If we stop adding the potassium cyanide when precipitation is just complete we can show by analysis that all the silver has been removed from the solution, and that it is all precipitated as cyanide. If now we continue to add potassium cyanide to the solution containing the precipitate the silver cyanide begins to redissolve, and when we have added just as much more potassium cyanide as was originally

required for the precipitation, shaking the mixture all the time, we find that all the silver cyanide has again gone into the solution. Clearly the solution now contains silver, and at the same time does not contain a recognisable amount of silver ions, since ordinary analytical tests fail to indicate their presence. The only means by which the silver can be precipitated consists in the addition of a sulphide solution, and even in this case the precipitation is not quite complete. If the liquid be allowed to evaporate, the salt  $KAg(CN)_2$  is obtained.

The reaction during precipitation is



or, in terms of the reacting ions,



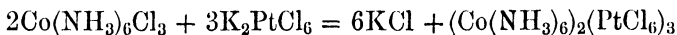
the  $K^+$  and  $NO_3^-$  ions remaining unchanged. From our study of the process of solution of the silver cyanide by addition of more potassium cyanide, we know further that one molecule of KCN causes one molecule of AgCN to dissolve, forming a compound yielding (analytically) no silver ions. Two potassium ions are still present, corresponding to the two stages of the reaction, and therefore it must be the cyanogen ion that has reacted with the silver cyanide to form this new compound.

Now, in all solutions containing ions the algebraic sum of the electric charges must be zero; and to balance the potassium ion introduced in the process of dissolving the silver cyanide, the compound which has been formed by the union of a cyanogen ion with a molecule of silver cyanide must have one negative charge. We might, therefore, conclude with a strong probability of being right that the compound formed was the complex ion  $Ag(CN)_2^-$ , or, allowing for the possibility of two or more molecules associating,  $Ag_m(CN)_{2m}$ , with  $m$  negative charges.

The method is simpler and perhaps more certain in the case of very stable complex ions. Here we find the complex ion persisting throughout a series of stable salts, such

as the ferro- and ferri-cyanides. The method of replacement has been successfully employed by Werner and his pupils in investigating a very large number of salts having complex kations containing respectively cobalt, chromium, platinum, iridium, nickel, iron, manganese, and other metals.

For example, cobaltic chloride forms with ammonia luteocobalt chloride,  $\text{Co}(\text{NH}_3)_6\text{Cl}_3$ . All three of the chlorine atoms are precipitated immediately by silver nitrate in the cold, leaving a solution containing luteocobalt nitrate,  $\text{Co}(\text{NH}_3)_6(\text{NO}_3)_3$ . The complex ion  $\text{Co}(\text{NH}_3)_6^{+++}$  forms a series of well-defined salts from which a solution of the free base  $\text{Co}(\text{NH}_3)_6(\text{OH})_3$  can be obtained. Further, the luteocobalt salts react with potassium platino- and platinichlorides yielding potassium chloride and the corresponding salts of the complex base. In these salts both anion and kation are complex. Thus with potassium platincyane the following reaction occurs:—



We thus have the strongest evidence on chemical grounds for the existence of the complex kation  $\text{Co}(\text{NH}_3)_6^{+++}$ .

When a salt formed from this complex ion loses one molecule of ammonia another series of salts is obtained, namely, the purpureo salts having the general formula  $(\text{Co}(\text{NH}_3)_5\text{R})\text{X}_2$ , in which R and X may be the same or different negative groups. In these only two of the acid residues form ions, so that if we allow the salt  $(\text{Co}(\text{NH}_3)_5\text{Cl})\text{Cl}_2$  to react with silver nitrate, two-thirds of the chlorine is precipitated while the remainder stays in solution. As in the case of the luteo salts, so also in this case the purpureo salts react with sodium or potassium platinichloride yielding salts of the type  $(\text{Co}(\text{NH}_3)_5\text{R})\text{PtCl}_6$ . This loss of ammonia accompanied by the absorption of the acid residue into the complex ion can be continued, yielding, for example, the compound  $(\text{Co}(\text{NH}_3)_4\text{Cl}_2)\text{Cl}$ , which dissociates into the monovalent complex kation  $\text{Co}(\text{NH}_3)_4\text{Cl}_2^+$  and the anion  $\text{Cl}^-$ , and next the compound  $\text{Co}(\text{NH}_3)_3\text{Cl}_3$ , which does not dissociate

at all. The analogous compound  $\text{Ir}(\text{NH}_3)_3\text{Cl}_3$  can be heated to boiling with sulphuric acid without losing  $\text{HCl}$ . Still another negative radical can be substituted for ammonia, giving compounds of the type  $(\text{M}(\text{NH}_3)_2\text{X}_4)\text{R}$ ,  $\text{R}$  being now a positive radical. The next stage is not known as yet, but very numerous examples of the final stage have been discovered, *e.g.*  $\text{Co}(\text{NO}_2)_6\text{K}_3$ . So far we have referred only to trivalent metals. Similar series of compounds have been discovered in the case of metals with valencies other than three, such as platinous and platinic compounds, nickelous compounds, etc.

Werner and Miolati (*Zeit. phys. Chem.*, **12**, 34 (1893); **14**, 506 (1894)) measured the electrical conductivity of solutions of a number of complex ammonia salts of platinum, cobalt and chromium, and showed that they could be divided in this way into classes yielding one, two, three, or four ions in addition to the complex ion. The following eight salts yielding one free ion gave values for the molecular conductivity at  $25^\circ$  ranging from 96.7 to 108.5:  $(\text{Pt}(\text{NH}_3)_3\text{Cl}_3)\text{Cl}$ ;  $(\text{Pt})(\text{NH}_3)_3\text{Cl}\text{Cl}$ ;  $(\text{Pt}(\text{NH}_3)\text{Cl}_5)\text{K}$ ;  $(\text{Pt}(\text{NH}_3)\text{Cl}_3)\text{K}$ ;  $(\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4)\text{K}$ ;  $(\text{Co}(\text{CO}_3)(\text{NH}_3)_4)\text{Cl}$ ; and the two stereoisomeric salts of the formula  $(\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4)\text{Cl}$  (Croceo- and flavo-cobalt chlorides).

Sixteen salts yielding two free ions gave values between 234.4 and 267.6, namely,  $(\text{Pt}(\text{NH}_3)_4\text{Cl}_2)$ ;  $(\text{Pt}(\text{NH}_3)_4\text{Cl}_2)\text{Cl}_2$ ;  $(\text{Pt}(\text{NH}_3)_4(\text{NO}_2)_2)(\text{NO}_3)_2$ ;  $(\text{PtCl}_4)\text{K}_2$ ;  $(\text{PtCl}_6)\text{K}_2$ ;  $(\text{Co}(\text{NO}_2)(\text{NH}_3)_5)(\text{NO}_2)_2$ ;  $(\text{CoBr}(\text{NH}_3)_5)\text{Br}_2$ ;  $(\text{CoCl}(\text{NH}_3)_5)\text{Cl}_2$ ;  $(\text{Co}(\text{NO}_3)(\text{NH}_3)_5)\text{Cl}_2$ ;  $(\text{Co}(\text{NO}_2)(\text{NH}_3)_5)\text{Cl}_2$  (two isomeric forms examined);  $(\text{CrCl}(\text{NH}_3)_5)\text{Cl}_2$ ;  $(\text{CrCl}(\text{NH}_3)_4\text{H}_2\text{O})\text{Cl}_2$ ;  $(\text{CrCl}(\text{NH}_3)_4\text{H}_2\text{O})\text{Br}_2$ ;  $(\text{CrCl}(\text{NH}_3)_4\text{H}_2\text{O})(\text{NO}_3)_2$ ;  $(\text{CrNO}_2(\text{NH}_3)_5)\text{Cl}_2$ .

The following seven salts yielding three free ions were examined, and gave values from 383.8 to 426.9:  $(\text{Co}(\text{NH}_3)_6)\text{Br}_3$ ;  $(\text{Co}(\text{NH}_3)_5\text{H}_2\text{O})\text{Br}_3$ ;  $(\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2)\text{Br}_3$ ;  $(\text{Co}(\text{NH}_3)_3(\text{H}_2\text{O})_3)\text{Cl}_3$ ;  $(\text{Co}(\text{NH}_3)_6)\text{Cl}_3$ ;  $(\text{Co}(\text{NH}_3)_6)(\text{NO}_2)_3$ ;  $(\text{Cr}(\text{NH}_3)_6)(\text{NO}_3)_3$ .

One salt giving four ions had the molecular conductivity



522·9. In each case the values are calculated for the molecule. The differences between the values for the different classes are so large that the method may be usefully applied to determine the number of ions formed in cases where chemical methods fail owing to analytical difficulties.

For Werner's method of classifying these compounds, and numerous references to original papers dealing with them, the reader is referred to Werner's *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie* (Braunschweig, F. Vieweg und Sohn, 1905), or the English translation, *New Ideas on Inorganic Chemistry* (Longmans, Green & Co., 1911).

## CHAPTER III

### THE IONIC MIGRATION METHOD

WHEN a current of electricity passes through an electrolyte the anions and kations do not, in general, move with equal velocities. Not taking account, for the moment, of the discharge of the ions at the electrodes, we see that if when one faraday passes through the solution the quantity of the anion in the neighbourhood of the anode increases by  $x$  gram-equivalents, then  $x$  is the fraction of the current that has been carried by the anions, and  $1 - x$  the fraction carried by the kations; and the difference between the total quantities of the two ion-forming constituents, including the portions discharged, in each of the two halves of the cell must be one equivalent. By analysing the solution in the two halves of the cell after passing the current we can therefore ascertain (1) what elements are present in the anion and the kation respectively, and (2) the quantities of these elements which are contained in one equivalent of the anion or the kation.

Here, then, we have an exact and unfailing method of recognising the formation of complex ions and determining their composition, provided that only one kind of anions and one kind of kations are present, *i.e.* that the complex formed is a fairly stable one.

For example, if we pass one faraday through a solution of potassium silver cyanide, we shall find that the solution at the anode contains one equivalent of silver in excess of the amount corresponding to the potassium content. The solution at the kathode contains two equivalents of silver less than the amount corresponding to the quantity of potassium present. One equivalent of silver has been deposited upon the kathode, so that including the discharged silver the

solution has lost one equivalent of silver with respect to the quantity of potassium present. The silver has therefore migrated to the anode as a constituent of a complex ion, and, further, one equivalent of this complex ion contains one equivalent of silver.

The ion  $K^+$  is the only kation present, and bearing in mind that the algebraic sum of the negative and positive charges in the solution must be equal to nothing and that one equivalent of the complex anion contains one atom of silver, we conclude that the formula of the complex salt must be  $(KAg(CN)_2)_x$  and that it must split into the ions  $xK^+$  and  $(Ag(CN)_2)_x$ , having  $x$  negative charges. Molecular weight determinations (M. Leblanc and A. A. Noyes, *Zeit. phys. Chem.*, **6**, 395 (1890)) enable us to decide in favour of the simple formula  $Ag(CN)_2'$  in which  $x = 1$ .

So far we have only considered the relative changes in the quantities of silver and potassium present in the two halves of the cell. By comparing these quantities with those originally present we can calculate the migration ratio for the anion ( $x$ ) and the kation ( $1 - x$ ). If the complex dissociates, then in a series of measurements with solutions of different strengths the apparent value of  $x$ , the migration ratio for the complex anion, calculated from the change in concentration of the metal it contains, will evidently diminish with diminishing concentration of the solution, since more and more of the metal functions as a kation instead of an anion.

In the years 1853–1859 Hittorf (*Pogg. Annalen*, **89**, 177 ; **98**, 1 ; **103**, 1 ; **106**, 337, 513) published a series of papers on the experimental study of migration in solutions of electrolytes during the passage of a current through them. His method was the one which is still often used, and consisted in passing a measured quantity of electricity through the solution and analysing the liquid in the neighbourhood of the anode or the kathode.

Hittorf first made preliminary experiments with copper sulphate in order to ascertain whether the migration ratio was affected by the current density in the solution, and

having found that it was not he proceeded to study the effect of concentration.

The following salts gave almost constant values for the migration ratio in solutions of concentration below 0.4N:  $\text{CuSO}_4$ ,  $\text{AgNO}_3$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{AgC}_2\text{H}_3\text{O}_2$ ,  $\text{KCl}$ ,  $\text{KBr}$ ,  $\text{KI}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{KNO}_3$ ,  $\text{KC}_2\text{H}_3\text{O}_2$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaCl}$ ,  $\text{NaNO}_3$ ,  $\text{NaC}_2\text{H}_3\text{O}_2$ .

At concentrations above 0.4N the transport numbers for some of the salts changed with the concentration, the number for the anion increasing with increasing concentration. There were one or two faintly marked exceptions to this rule, where the number changed in the opposite direction.

Many other electrolytes, however, were found to give quite different results from any of the above salts, and notably the iodides and chlorides of cadmium and zinc. For example, Hittorf gave the following figures for  $\text{CdI}_2$  and  $\text{CdCl}_2$  :—

## CADMIUM IODIDE.

Temperature.	Parts water to one part salt.	Transport numbers.	
		Cd.	I.
—	1.8313	—0.258	1.258
11	3.04	—0.192	1.192
11.8	4.277	—0.148	1.140
11.2	18.12	0.069	0.931
—	69.60	0.358	0.642
10	166.74	0.387	0.613

## CADMIUM CHLORIDE.

Temperature.	Parts water to one part salt.	Transport numbers.	
		Cd.	Cl.
10.6	1.2724	—0.015	1.015
9.8	1.2692	—0.016	1.016
6.8	1.2848	—0.014	1.014
7	1.9832	0.127	0.873
9.6	2.7588	0.221	0.779
9.5	3.3553	0.228	0.772
?	5.7611	0.256	0.744
7.8	98.708	0.275	0.725
10.5	191.82	0.292	0.708

Hittorf also studied potassium ferrocyanide, potassium silver cyanide, sodium platinichloride, potassium aurichloride, and the salts  $\text{HgCl}_2$ ,  $2\text{KCl}$ ,  $2\text{HgCl}_2$ ,  $2\text{KCl}$ ,  $4\text{HgCl}_2$ ,  $2\text{KCl}$  and  $\text{CdI}_2$ ,  $2\text{KI}$ , and showed that in each case the alkali metal forms the kations and moves towards the kathode, while a portion of the nobler metal moves with the acid radicle towards the anode. In the cases of potassium ferrocyanide, potassium silver cyanide, and sodium platinichloride the gain in the metal of the anion at the anode or the loss at the kathode compared with the amount of alkali metal present was exactly an integral number of equivalents for each equivalent of silver deposited in the voltameter in series with the cell, showing that the salt split solely into kations of the alkali metal and complex anions containing the nobler metal.

In the case of potassium aurichloride and the other salts mentioned above the loss at the kathode was less than would have been the case had the complex ion been quite stable, and Hittorf therefore concluded that dissociation had occurred, and according to the theory of the time this was supposed to be due to the influence of the electric current.

In order to make the foregoing clearer we shall consider two numerical examples from Hittorf.

1. *Potassium ferrocyanide.*

13.7207 grams of solution before electrolysis gave 2.0505 grams of potassium sulphate and 0.4769 gram of ferric oxide. 23.3087 grams of solution from the anode chamber after electrolysis gave 3.2445 grams of potassium sulphate and 0.8586 gram of ferric oxide. During the passage of the current 0.5625 gram of silver was deposited on the kathode in the voltameter.

Using Hittorf's values for the equivalents we find that the anode solution after electrolysis contained 1.4585 grams of potassium and 0.60096 gram of iron. In potassium ferrocyanide 1.4585 grams of potassium are equivalent to 0.5209 gram of iron, or, taking the figures from the analysis of the solution before electrolysis, 0.5281 gram of iron.

There was thus an excess of iron in the anode chamber over the amount corresponding to the amount of potassium present of  $0.60096 - 0.5281$  gram,  $= 0.07286$  gram  $= 0.002602$  equivalent. The reduced silver,  $0.5625$  gram, is  $0.00521$  equivalent. It follows, therefore, that the valency of an ion containing one equivalent of iron is  $0.00521/0.002602$ , or the valency of the complex ion containing one atom of iron is  $2 \times 0.00521/0.002602 = 4$ , almost exactly.

Similarly, the deficit in potassium corresponding to two equivalents of iron is four gram atoms. Hence, if the complex ion is not associated, its formula must be  $\text{Fe}(\text{CN})_6'''$ , and the salt on dissociation yields this complex anion and four potassium ions.

Further, we may calculate the transport numbers for the anion and the kation in the usual way. Before electrolysis,  $13.7207$  grams of the solution contained  $1.5341$  grams of KCN and  $0.644$  gram of  $\text{Fe}(\text{CN})_2$ . After electrolysis,  $23.3087$  grams of the anode solution contained  $2.4282$  grams of KCN and  $1.1591$  grams of  $\text{Fe}(\text{CN})_2$ . No gas is produced at the anode until all the  $\text{Fe}(\text{CN})_6'''$  has been oxidised to  $\text{Fe}(\text{CN})_6''$ , when oxygen begins to be evolved. The electrolysis was stopped as soon as the first bubbles of oxygen were seen, and the amount of cyanogen in addition to that included in the above weights of KCN and  $\text{Fe}(\text{CN})_2$  was calculated from the weight of silver deposited in the voltameter. Its weight is  $0.5625 \times \frac{26}{108} = 0.1353$  gram. The anode solution therefore contains  $23.3087 - 2.4282 - 1.1591 - 0.1353 = 19.5861$  grams of water.

Before electrolysis this amount of water would have corresponded to  $1.5641$  grams of potassium, so that the loss of potassium is  $1.5641 - 1.4585 = 0.1056$  gram. The weight of potassium corresponding to  $0.5625$  gram of silver is  $0.204$  gram. We thus find that the transport number for the kation (K) is  $0.1056/0.204 = 0.518$ , while similarly that for the anion is  $0.482$ .

## 2. Potassium cadmium iodide.

This salt has the composition which is represented by the formula  $\text{K}_2\text{CdI}_4$ .

The solution was prepared by dissolving equivalent amounts of cadmium iodide and potassium iodide in a small quantity of water. 15.8994 grams of solution gave 16.102 grams of silver iodide, 3.4367 grams of potassium nitrate, and 2.223 grams of cadmium oxide. 24.6033 grams of solution from the kathode vessel after electrolysis gave 24.6147 grams of silver iodide, 6.2027 grams of potassium nitrate, and 2.8352 grams of cadmium oxide. During electrolysis 0.9784 gram of silver was deposited in the voltameter.

In the original solution 6.2027 grams of potassium nitrate would correspond to 3.4833 grams of cadmium, while the amount of cadmium found was 2.4808 grams. The deficit of cadmium is therefore  $3.4833 - 2.4808 = 1.0025$  grams cadmium, or 0.0179 equivalent. The silver deposited in the voltameter was 0.00906 equivalent, and this amount of cadmium was also deposited upon the kathode. The deficit due to migration was therefore  $0.0179 - 0.00906 = 0.00884$  equivalent.

Thus the cadmium moved towards the anode during the electrolysis, and if it all behaved alike, the valency of the ion containing an atom of cadmium (two equivalents) was  $0.00906/0.00884 \times \frac{1}{2} = 2.05$ . The salt thus forms the ions  $2K^+$  and  $CdI_4^{2-}$ . The same result may be obtained by calculating from the quantities of silver iodide and cadmium oxide or from the silver iodide and potassium nitrate found.

Calculating the migration ratios as before, we find—

$$u_A \text{ (ratio for the anion)} = 0.31$$

$$u_K \text{ (ratio for the kation by difference)} = 0.69$$

It is interesting to calculate the fraction of the current carried by each constituent of the solution. We may carry this out as follows:—

15.899 grams of the original solution contained 5.645 grams of potassium iodide and 6.343 grams of cadmium iodide, and hence 3.911 grams of water. The cadmium content of this solution is 1.946 grams.

24.6033 grams of the kathode solution after electrolysis

contained 8.086 grams of cadmium iodide, 10.188 grams of potassium iodide, and hence 6.329 grams of water. The cadmium content of this solution was 2.482 grams.

6.329 grams of water in the original solution corresponds to 3.149 grams of cadmium. Hence the decrease in the cadmium content of the kathode solution compared with the original solution is  $3.149 - 2.481 = 0.668$  gram or 0.01189 equivalent.

0.00906 equivalent of cadmium was deposited upon the kathode, so that the loss due to migration was  $0.01189 - 0.00906 = 0.00283$  equivalent.

Thus the migration ratio, assuming the cadmium to be positively charged, is  $-0.00283/0.00906 = -0.312$ .

Similarly, the values for the iodine and potassium respectively are 0.613 and 0.712.

These figures really represent the fractions of the current that travel in company with the respective constituents through the solution. Comparing the values for cadmium and iodine, we see that the ratio for iodine is almost exactly double that for the cadmium, showing that the two equivalents of iodine accompany each equivalent of cadmium, or, in other words, that the formation of the ion  $\text{CdI}_4''$  is practically complete.

In more dilute solutions the behaviour was less simple. Thus, in a solution containing one part of the salt to 58.72 parts of water, Hittorf found the migration ratios

Iodine . . . . .	0.560
Cadmium . . . . .	0.00
Potassium . . . . .	0.459

so that the cadmium had apparently not moved at all, or different portions of it had moved in opposite directions. Hittorf therefore concluded that the "double salt" dissociated as the dilution increased.<sup>1</sup>

It is worthy of remark that these results were arrived at

<sup>1</sup> McBain (*Zeit. Elektrochem.*, **11**, 222 (1905)) has shown that in weaker solutions the ion  $\text{CdI}_3'$  is formed.



in days when no word had been heard of the modern theory of electrolytic dissociation, and before any quantitative expression had been found for the law of mass action.

In later years more exact measurements of migration ratios were made, and subsequently methods were invented by which the speed of the ions could be directly observed.

Thus A. A. Noyes (*Technology Quarterly*, **17**, 4, Dec., 1904) made very exact measurements of the migration ratios for the following salts: KCl, NaCl, HCl, HNO<sub>3</sub>, AgNO<sub>3</sub>, Ba(NO<sub>2</sub>)<sub>2</sub>, K<sub>2</sub>SO<sub>4</sub>, CuSO<sub>4</sub>, LiCl, CdSO<sub>4</sub>, BaCl<sub>2</sub>, and the halides of several other divalent metals. For the eight salts first mentioned the ratio does not change to the extent of one per cent. of its value while the concentration is increased from 0.02N to 1.0N. In the solutions of LiCl, CdSO<sub>4</sub>, BaCl<sub>2</sub>, and other chlorides of the heavy metals, the ratio for the anion increases with increasing concentration.

Direct measurements of the velocity of a number of ions have been made by Whetham (*Phil. Trans.*, A, 1893, 337), Masson (*Zeit. phys. Chemie*, **29**, 501 (1899)), Steele (*Zeit. phys. Chemie*, **40**, 689 (1902)), and others. Whetham and Masson worked with solutions in jellies, but Steele succeeded in dispensing with the jelly. The effect of the gelatine upon the velocity is small. The results of these measurements showed that the velocity is only completely independent of the concentration in the case of a few salts, but in the cases mentioned above the variation is only slight.

All succeeding work has tended to ratify the general results of the rather less refined experiments of Hittorf.

The interpretation of the variability of the ionic velocities has been the subject of much controversy. Noyes pointed out that a disturbing influence, such as alteration in the ionic friction with change in concentration which changes the velocity of one ion, should also change that of the other to about the same extent, and thus be nearly without effect upon the ratio. He therefore concluded that the only possible cause of variability in the ratio was the formation of complex ions. Steele (*Phil. Trans.*, A, 1902, 105) in a

review of the whole subject of migration in relation to complex formation came to the same conclusion.

On the other hand, Riesenfeld and Reinhold (*Zeit. phys. Chemie*, **66**, 672) consider the variation in the migration ratio to be due to hydrate formation.

Without entering into a discussion of the subject it may be said that change in the degree of hydration of the ions does probably cause small deviations from constancy in the migration ratio, but that this does not affect the conclusions that have been drawn from the study of migration in the case of comparatively stable complexes.

The bearing of the hydrate theory in general upon the theory of complex ions will be discussed in Appendix I.

## CHAPTER IV

### THE DISTRIBUTION METHOD

WHEN a substance dissolves in two very slightly miscible liquids in contact with one another the ratio of the concentrations of molecules of the same kind in the two layers is constant. This was shown experimentally for various substances by Berthelot and Jungfleisch (*Ann. chim. phys.*, (4) **26**, 396 (1872)), and may be proved theoretically by considering the case in which the solute is a gas (see, for example, Nernst, *Theoretische Chemie*, 5<sup>te</sup> Auflage, p. 490). When the two layers are in equilibrium the gaseous pressure of the solute in the surrounding space must be the same for both. This pressure is proportional to the concentration in each solvent, so that if the gaseous pressure be  $p$  and the concentrations  $c_1$  and  $c_2$  we have

$$p = k_1 c_1 = k_2 c_2$$

and hence

$$\frac{c_1}{c_2} = \frac{k_2}{k_1} = \text{constant}$$

This relation holds good for every kind of solute molecules that may be present, and for each kind it is independent of the others.

Thus, if a substance dissolves to a measurable extent in the two liquids but consists mainly of different molecules in the two layers, the total concentrations are no longer proportional to one another. In this case, as before,

$$c_1 = k c_2$$

when  $c_1$  and  $c_2$  represent the concentrations of molecules of one kind. Suppose that in the liquid (2) the substance

exists mainly in the form of double molecules: we then obtain from the law of mass-action

$$c_2^2 = k'c_3$$

where  $c_3$  is the concentration of double molecules. If the amount of substance present as single molecules is small (*i.e.* if  $k'$  is small) the concentration as determined analytically is practically  $c_3$ , and we thus find

$$c_1 = k\sqrt{k'c_3} = K\sqrt{c_3}$$

Thus Nernst (*Zeit. phys. Chem.*, **8**, 110 (1891)) determined the distribution coefficient of benzoic acid between water and benzene at various concentrations, and found that the concentration in the water layer was proportional to the square root of the concentration in the benzene layer, showing that the benzoic acid in the benzene consisted mainly of double molecules, in agreement with the freezing-point determinations of Beckmann (*Zeit. phys. Chem.*, **2**, 729 (1888)). Beckmann's results indicated a slight dissociation into single molecules in weak solutions, and the distribution experiments showed the same result. Since benzoic acid dissociates electrolytically to a small extent in the water layer the amount of dissociated acid must be subtracted from the total amount in order to obtain the true concentration of undissociated molecules. Various other substances were examined by Nernst in this way, and in each case the results were in agreement with those obtained by the freezing-point methods.

Again, if we know the distribution ratio of a substance between two liquids and find that it apparently changes on introducing a small quantity of a solute which dissolves only in one, we are able to conclude that the two solutes form a compound, and we can tell how much of the first one has combined with the second. This method has been used for the investigation of certain cases of complex formation.

Thus Roloff (*Zeit. phys. Chem.*, **13**, 341 (1894)) studied the reaction which occurs in aqueous solution between bromine and potassium bromide, by shaking various solutions

of potassium bromide with a strong solution of bromine in carbon disulphide. A sufficiently large quantity of this solution was used to ensure that the change in its concentration due to the withdrawal of bromine by the potassium bromide solutions should be small. The solution was first shaken with water, and the concentration of bromine in the water layer determined. The successive solutions of potassium bromide were then shaken, the amount of bromine in the water layer being found by titration in each case. Finally, the carbon disulphide solution was shaken with water again, and the change in the amount of bromine withdrawn noticed.

From the quantities of bromine in the water layer in the first and last experiments the concentrations of free bromine in the potassium bromide solutions were obtained by interpolation, the amount removed in each experiment being known. Calling these concentrations  $D$  and the concentrations found by titration  $B$ , it follows that in any experiment  $B - D$  gram molecules per litre have reacted to form a complex with the potassium bromide. Thus by this method it was unnecessary to determine the distribution ratio, and the awkward determination of bromine in a strong carbon disulphide solution was avoided.

In order to calculate the dissociation constant of the complex ion we must adopt a hypothetical scheme representing the reaction; and conversely, since the complex ion must have a dissociation constant, it follows that if the law of mass-action holds good the scheme which gives constant values for the dissociation constant is the one which truly represents the reaction.

Roloff proceeded to calculate the dissociation constant for the complex ion on the assumption that it had the constitution  $\text{Br}_3'$ , and found constant values for the dissociation constant. On this hypothesis the reaction between the bromine ion and the molecule of bromine must be represented by the equation



whence we obtain

$$[\text{Br}_3'] = K[\text{Br}_2][\text{Br}']$$

Calling the initial concentration of bromine ions  $A$  we have

$$[\text{Br}_3'] = B - D$$

$$[\text{Br}_2] = D$$

$$[\text{Br}'] = A - (B - D)$$

This calculation does not take account of the electrolytic dissociation of the potassium bromide. We are assuming either (1) that the electrolytic dissociation is complete, which is not far from the actual state of affairs, or (2) that the  $\text{Br}_2$  molecules combine equally well with the bromine ions and with the undissociated potassium bromide. Further, the undissociated complex salt, if any, must behave like the complex ion. We thus obtain

$$K = \frac{D(A - (B - D))}{B - D}$$

Using these expressions the following values were found:—

TEMPERATURE = 32.6° C.

D.	B.	A.	K.
0.0264 (water)	—	—	—
0.0261	0.1111	0.250	0.0508
0.0259	0.0686	0.125	0.0500
0.0257	0.0472	0.0625	0.0488
0.0255 (water)	—	—	—

TEMPERATURE = 32.7° C.

D	B.	A.	K.
0.0318 (water)	—	—	—
0.0316	0.1273	0.250	0.0510
0.0315	0.0795	0.125	0.0505
0.0313	0.0555	0.0625	0.0498
0.0312 (water)	—	—	—

Another set of measurements was made in which the

concentration of the bromine was altered by adding measured quantities of carbon disulphide while the potassium bromide concentration remained constant. The results are given below.

TEMPERATURE = 32.6° C.

D.	B.	A.	K.
0.0477 (water)	—	—	—
0.0475	0.1078	0.125	0.0510
0.0236	0.0646	0.125	0.0501
0.0157	0.0452	0.125	0.0508
0.0117	0.0362	0.125	0.0480
0.0116 (water)	—	—	—

It is thus clear that the scheme



must be taken as representing very closely the real state of affairs.

Roloff concluded that the free bromine must attach itself to the undissociated potassium bromide, as well as to the bromine ions. As the salt is nearly completely dissociated this has little bearing upon the formation of the complex ion as deduced from the results. This work, therefore, affords very strong evidence of the formation of the complex ion  $\text{Br}_3'$ , and also gives us information as to its stability.

Further experiments on the subject were made by Worley (*Trans. Chem. Soc.*, **87**, 1107 (1905)), who determined the solubility of bromine in solutions of potassium bromide, and also measured the concentration of free bromine in unsaturated solutions by getting the solutions into equilibrium with a quantity of water separated from the solution by an air-space which was partially evacuated. In each case the results showed that in weak solutions the compound  $\text{KBr}_3$  was formed, while in more concentrated solutions small quantities of a higher polybromide were present.

The distribution method was also employed by Jakowkin (*Zeit. phys. Chem.*, **13**, 539 (1894); **18**, 585 (1895); **20**, 19 (1896)) in investigating the complex-formation in solutions of iodine in potassium iodide. Jakowkin measured the distribution of iodine between water and carbon disulphide and determined the iodine in the carbon disulphide layer in contact with the complex solution. The constant

$$k = \frac{[\text{KI}][\text{I}_2]}{[\text{KI}_3]}$$

calculated from his first results varied somewhat with the concentrations of the components. Further experiments showed, however, that the distribution ratio is not quite independent of the concentrations, the ratio  $\frac{C_{(\text{CS}_2)}}{C_{(\text{H}_2\text{O})}}$  rising as the concentration increases. This indicated that association occurs to some extent in the carbon disulphide layer. The values of the distribution constant were therefore plotted against the concentration, so that the free iodine in the aqueous layer could be calculated with accuracy from the concentration in the carbon disulphide layer. On making this correction thoroughly concordant values were obtained for the constant over a wide range of concentrations. Nearly the same value was obtained with solutions of lithium, sodium, and barium iodides. Hydriodic acid solutions gave a slightly lower value.

These experiments thus show that the compound  $\text{KI}_3$  is formed in solutions of iodine and potassium iodide, and this dissociates yielding the complex ion  $\text{I}_3'$ . In the light of this knowledge such solutions were used by Abegg and Maitland (*Zeit. Elektrochemie*, **12** (1906)) in order to measure the electrolytic potential of iodine.

It may be noted that, as in the case of Roloff's work, Jakowkin assumes that the iodine ion and the undissociated potassium iodide act similarly.

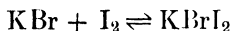
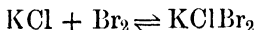
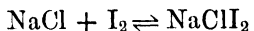
Jakowkin also repeated Roloff's work with potassium bromide and bromine, using carbon tetrachloride in place of



carbon disulphide, and found concordant values for the constant

$$k = \frac{[\text{KBr}][\text{Br}_2]}{[\text{KBr}_3]}$$

the values being a little higher than Roloff's. He also studied the equilibria



and in each case the experimental results showed satisfactory agreement with the law of mass-action in accordance with the above schemes, thus showing the existence of the ions  $\text{ClI}_2'$ ,  $\text{ClBr}_2'$ ,  $\text{BrI}_2'$ .

When the concentration of the dissolved salt is considerable it exerts an appreciable effect upon the solubility of the free halogen, and hence upon the distribution coefficient, which is the ratio of the solubilities in the two solvents. This effect was studied by Setschenoff (*Zeit. phys. Chem.*, **4**, 117 (1889)), and the concentrations obtained using the distribution coefficient were corrected in accordance with the expression worked out by him. It was found, however, that when the concentration of the halogen was largely increased the values of the dissociation constant fell somewhat.

The only explanation that could be offered for this was that higher polyiodides are formed. Wildermann (*Zeit. phys. Chem.*, **11**, 407 (1893)) arrived at the same conclusion from a study of the solubility of bromine in potassium bromide solutions.

A very large number of solid tri-halides of the alkali metals has been obtained including both simple and mixed salts (Johnson, *Trans. Chem. Soc.*, **31**, 249 (1877); Wells and Penfield, *Zeit. anorg. Chem.*, **1**, 85 (1892); Wells and Wheeler, *ibid.*, **1**, 442 (1892)), and numerous examples of the formation of polyiodides of organic bases are known. Further, Wells and Wheeler (*loc. cit.*) obtained the solid compounds  $\text{CsI}_5$ ,  $\text{CsBr}_5$ , etc., and later Abegg and Hamburger

(*Zeit. anorg. Chem.*, **50**, 403 (1906)) prepared numerous polyiodides of ammonium and the alkali metals, the two containing the largest possible amount of iodine at 25° being  $\text{RbI}_9$  and  $\text{CsI}_9$ . Dawson and his co-workers (Dawson and Gawler, *Trans. Chem. Soc.*, **81**, 524 (1902); Dawson and Goodson, *ibid.*, **85**, 796 (1904); Dawson, *ibid.*, **85**, 467 (1904)) showed the existence of a similar series of compounds in solution in nitrobenzene and other organic solvents, the composition of the compounds in the solutions being arrived at by means of distribution experiments.

The distribution method was also used by Dawson and McCrae (*Trans. Chem. Soc.*, 1901, 496, 1072) in order to examine the constitution of the cuprammonium ion in solution. The distribution coefficient for ammonia between water and chloroform was first determined. This is nearly independent of the concentration, but shows a very slight variation. To correct for this the coefficient was found by interpolation for each concentration used. Thus by measuring the concentration of ammonia in the chloroform layer the concentration of free ammonia in the aqueous layer was calculated. The total amount of ammonia in both layers being known, the quantity of "fixed" ammonia in the aqueous layer was found, and hence the number of molecules of ammonia which were combined with each molecule of copper salt. Experiments with copper sulphate at 10° C. and at 30° C. respectively showed that in each case this number was about 3.6. The true number must obviously be an integer, and Dawson and McCrae considered the most probable explanation to be that the salt  $\text{CuSO}_4 \cdot 4\text{NH}_3$  is formed, and undergoes partial dissociation.

## CHAPTER V

### THE SOLUBILITY METHOD

WHEN a binary electrolyte is dissolved in water the molecules dissociate in the solution according to the scheme



where AB represents the undissociated molecule of salt, A' the negatively charged ion, and B' the positively charged one.

If we keep on adding solid salt to the liquid a stage is finally reached when no more solid will dissolve, and the solution is saturated with the salt. This state of affairs is determined by the equilibrium



and the system has two degrees of freedom, the vapour phase being absent. At a given temperature and pressure, therefore, the concentration of AB molecules in the solution is fixed if the solid salt is present. The effect of changes in the pressure of the atmosphere upon the solubility of a salt is negligible, so that practically the saturation concentration of undissociated molecules is affected only by temperature.

In a saturated solution the concentrations of the ions A' and B' must be such that

$$k[A'][B'] = [AB]$$

so that in a saturated solution the product  $[A'][B']$  is also constant. This product is called the *Solubility Product*.

The solubility of a salt in water is therefore made up of two parts, namely, (1) the concentration of the undissociated molecules, and (2) the concentration of one of the ions produced from them.

If to a saturated solution of an electrolyte another electrolyte be added, having one ion ( $A'$ ) in common with the first, without altering the volume of the solution, the value of  $[A']$  tends to be increased. This causes some of the ions  $A'$  to combine with the ion  $B\cdot$  forming undissociated salt molecules,  $AB$ . This in its turn is precipitated, since the solution is already saturated with respect to  $AB$ . The total result is therefore that the solubility of an electrolyte is lowered by adding to the solution a second electrolyte having one ion in common with the first electrolyte.

We shall now proceed to calculate the solubility of a slightly soluble electrolyte in a solution previously containing a second electrolyte at a given concentration, containing an ion in common with the first electrolyte. This calculation was first worked out and applied by Nernst.

Let  $s$  be the solubility of the slightly soluble electrolyte in water,  $\gamma$  its degree of dissociation in saturated solution, and  $x$  the concentration of the common ion in the added electrolyte—that is, the electrolyte already in the solution. If this is a highly dissociated substance the value of the constant

$$k = \frac{[A'] [B\cdot]}{[AB]}$$

will be high, and a small change in  $[AB]$  will correspond to a large alteration in the value of  $[A']$  or  $[B\cdot]$ . Thus the addition of a relatively small amount of the (slightly soluble) electrolyte producing either  $A'$  or  $B\cdot$  ions will not materially affect the degree of dissociation of the added electrolyte, so that in the mixed solution we may take the concentration of either ion due to this electrolyte as equal to  $x$  without serious error.

If  $\gamma_1$  be the degree of dissociation of the slightly soluble salt in the mixed solution which is saturated with it, and  $\eta$  its solubility, *i.e.* its concentration in this solution, we have

$$\gamma_1 \eta (\gamma_1 \eta + x) = (s\gamma)^2$$

Solving for  $\eta$  we obtain

$$\eta = -\frac{x}{2\gamma_1} + \sqrt{\frac{x^2}{4\gamma_1^2} + s^2\left(\frac{\gamma}{\gamma_1}\right)^2} \quad . \quad . \quad (1)$$

This is the original formula of Nernst. The equation, however, contains two unknown quantities,  $\gamma_1$  and  $\eta$ . From the values of  $\gamma$  and  $s$  for the water solution it is possible to find approximately the value of  $\gamma_1$ , and so to calculate  $\eta$ .

This method was tested experimentally by A. A. Noyes (*Zeit. phys. Chem.*, **6**, 241 (1890)), who determined the solubility of silver bromate in solutions of silver nitrate and potassium bromate respectively. The following table gives the values found by Noyes:—

Conc. of added salt.	Solubility of $\text{AgBrO}_3$ in $\text{AgNO}_3$ .	Solubility of $\text{AgBrO}_3$ in $\text{KBrO}_3$ .	Solubility calculated.
0	0.00810	0.00810	—
0.00850	0.00510	0.00519	0.00504
0.0346	0.00216	0.00227	0.00206

The agreement between the observed values and those calculated from the equation is quite good, and as the determination of  $\gamma_1$  was accomplished by means of a rather inexact extrapolation the small differences may be due to error introduced in this way.

A simpler and more exact method of performing the calculation is the following, which was worked out and used by the author (*Trans. Faraday Soc.*, **5**, 225 (1910)) in calculating the solubility of silver acetate in silver nitrate and sodium acetate solutions.

Solving the equation

$$\gamma_1\eta(\gamma_1\eta + x) = (s\gamma)^2$$

for  $\gamma_1\eta$  instead of for  $\eta$  we obtain

$$\gamma_1\eta = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + (s\gamma)^2}$$

Now, since the solubility  $\eta$  is made up of the constant

concentration of the undissociated salt which is given by  $s(1 - \gamma)$  and the concentration of the ion which is not common to the two salts, namely,  $\gamma_1\eta$ , we have

$$\eta = s(1 - \gamma) + \gamma_1\eta$$

Substituting the value of  $\gamma_1\eta$  in this equation, we find

$$\eta = -\frac{x}{2} + \sqrt{\frac{x^2}{4} + (s\gamma)^2} + s(1 - \gamma) \quad . \quad (2)$$

We thus obtain  $\eta$  in terms of  $x$ ,  $s$ , and  $\gamma$ , all of which can be accurately determined.

The following table shows the values obtained by recalculating Noyes' results in this way:—

Conc. of added salt.	Solubility of AgBrO <sub>3</sub> in AgNO <sub>3</sub> .	Solubility of AgBrO <sub>3</sub> in KBrO <sub>3</sub> .	Calculated solubility.
0	0.00810	0.00810	—
0.00850	0.00510	0.00519	0.00510
0.0346	0.00216	0.00227	0.00223

The agreement is thus improved by using formula (2). The author also found good agreement between the calculated experimental values in the case of solutions of silver acetate in silver nitrate.

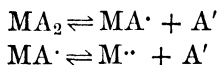
Noyes also showed that it follows from the law of mass action that the solubility of an electrolyte must be increased by addition of another electrolyte not having a common ion, and developed an expression for the increase, assuming that the two electrolytes were equally dissociated. He also examined the effect of ternary electrolytes upon the solubility of binary ones having a common ion. Thus by calculating the value of  $x$ , the concentration of the common ion due to the added electrolyte, from the experimentally determined solubility of the binary salt, he was able to find numbers representing the degree of dissociation of the ternary electrolyte assuming that it dissociated according to the scheme



Later, Noyes (*Zeit. phys. Chem.*, **9**, 626 (1892)) showed

how to calculate the depression in the case of two ternary electrolytes, assuming that dissociation occurred according to the same scheme, and in order to test the accuracy of his expression he measured the solubility of lead chloride in solutions of magnesium, calcium, zinc, and manganese chlorides. Fair agreement was found between the observed and calculated values when the concentration of the added salt was not greater than 0.1 N. Above this concentration the solubilities found were higher than the calculated values.

It is now known that the dissociation of a ternary electrolyte occurs in two stages according to the scheme



This does not affect the accuracy of Noyes' calculations, however, for on multiplying together the two constants

$$k_1 = \frac{[\text{MA}\cdot][\text{A}']}{[\text{MA}_2]} ; k_2 = \frac{[\text{M}\cdot\cdot][\text{A}']}{[\text{MA}\cdot]}$$

we obtain 
$$k_1 k_2 = K = \frac{[\text{M}\cdot\cdot][\text{A}']^2}{[\text{MA}_2]}$$

so that the product  $[\text{M}\cdot\cdot][\text{A}']^2$  is constant as assumed in the calculation.

Although there was no doubt that in solutions of concentration not greater than 0.1 N. the solubility depression follows the path indicated by the theory of electrolytic dissociation and the law of mass action, the agreement thus far obtained between theory and experiment was not all that could be desired. Two possible causes were suggested for the divergencies, namely, (1) untruthfulness of the law of mass action, and (2) inaccuracy in the (approximately determined) degrees of dissociation for the slightly soluble salt in the mixed solution. In order to find out to which of these causes the unsatisfactory character of the agreement was due, Noyes and Abbott (*Zeit. phys. Chem.*, **16**, 125 (1895)) devised a method of calculating without approximation from solubility experiments the value of the degree of dissociation of a salt in solution in water. If the values

obtained in this way agree with those obtained from conductivity measurements, it follows that the discrepancies observed in previous experiments must have been due to inaccuracy in the approximate calculation of the values of  $\gamma_1$ , and that the salts in solution do strictly obey the law of mass action.

The method is as follows: Let  $s$  and  $s'$  be the solubilities of two salts in pure water and  $\eta$  and  $\eta'$  those when both salts are present in excess. Let  $\gamma$ ,  $\gamma'$ ,  $\gamma_1$ , and  $\gamma_1'$  be the corresponding degrees of dissociation. Then, since the concentration of the undissociated molecules of each salt is constant in all saturated solutions, we have

$$\begin{aligned}s(1 - \gamma) &= \eta(1 - \gamma_1) \\ s'(1 - \gamma') &= \eta'(1 - \gamma_1')\end{aligned}$$

Further, since the solubility products are also constant,

$$\begin{aligned}(s\gamma)^2 &= \eta\gamma_1(\eta\gamma_1 + \eta'\gamma_1') \\ (s'\gamma')^2 &= \eta'\gamma_1'(\eta'\gamma_1' + \eta\gamma_1)\end{aligned}$$

These four equations contain only four unknown quantities—the degrees of dissociation. These can therefore be calculated from the experimental values for the solubilities, and they include the values for solutions of the two salts in pure water.

Experiments were conducted by Noyes and Abbott with the three sparingly soluble salts,  $\text{TiCl}$ ,  $\text{TiSCN}$ , and  $\text{TiBrO}_3$ . The solubility of each salt was determined in water, and then the solubilities were measured in the three possible solutions saturated with respect to a pair of the salts. The conductivity of each salt was measured in its saturated solution in water, and the dissociation degrees were calculated. The following table shows the values found:—

Salt.	Mean percentage dissociation from solubility.	Dissociation from conductivity.
$\text{TiCl}$	$86.5 \pm 0.3$	$86.6 \pm 0.1$
$\text{TiSCN}$	$86.6 \pm 0.3$	$85.6 \pm 0.1$
$\text{TiBrO}_3$	$90.2 \pm 0.4$	$89.0 \pm 0.1$



Thus we have strong reason to believe that the law of mass action is obeyed by salts in dilute solution, and that the values of  $\gamma$  obtained by conductivity measurements are also correct.

Good agreement should therefore be obtained between observed and calculated results by using equation (2), and as we have already seen, this is the case.

These equations only hold good for dilute solutions in which ionisation occurs normally, that is, when no complex ions are formed. Any departure from the value calculated by the above methods indicates that a disturbance of the simple conditions assumed in developing them has occurred. The only known cause of an increase of the solubility of a salt above the theoretical value as calculated is the formation of complex ions. Kendall (*Proc. Roy. Soc., A*, **85**, 200 (1911)) showed that in the case of certain acids the solubilities in mixed solutions show considerable divergences from the theoretical values, but in every case this can be accounted for by the change in the solubility of the undissociated compounds caused by the solvent effect of the acids upon one another. In dilute solutions such divergences do not amount to more than a few per cent. of the solubility.

An example of the identification of a stable complex ion from a study of the solubility of a very sparingly soluble salt in a solution of another electrolyte has already been given in Chapter II, where we saw that one gram molecule of potassium cyanide in solution dissolves exactly (within the limits of analytical error) one molecule of silver cyanide, yielding a solution containing potassium ions, but practically no silver ions. Hence a complex ion must have been formed whose composition is represented by the formula  $\text{Ag}(\text{CN})_2'$ . If we knew the concentrations  $[\text{Ag}']$  and  $[\text{CN}']$  we could calculate the value of the dissociation constant

$$k = \frac{[\text{Ag}'][\text{CN}']}{[\text{Ag}(\text{CN})_2']}$$

This has been done by Bodländer and Eberlein (*Zeit. anorg.*

*Chem.*, **39**, 197 (1904)) by methods which will be discussed in succeeding chapters.

Similarly, four gram molecules of potassium cyanide would dissolve one gram molecule of ferrous cyanide, yielding potassium ferrocyanide,  $K_4Fe(CN)_6$ , in which no ferrous ions or cyanogen ions are recognisable, but only potassium ions and the complex ion  $Fe(CN)_6^{4-}$ .

In the cases of these exceptionally stable complexes one or more of the reacting ions disappears completely so far as analytical methods—including solubility determinations—are concerned, and can only be identified by physical means which will be described in the next chapter.

We can sometimes gain a qualitative knowledge of the concentration of an ion present only in minimal amount by finding a reagent with which it forms a compound so insoluble that even with the small quantity of the ion present we can cause the solubility product for the insoluble compound to be exceeded. Thus by adding excess of potassium chloride to an ammoniacal solution containing silver we can cause some of the silver to be precipitated as chloride. On adding more ammonia the precipitate is re-dissolved. Potassium chloride cannot precipitate a visible amount of silver chloride from its solution in potassium cyanide, but addition of an alkaline sulphide causes the much more insoluble silver sulphide to separate.

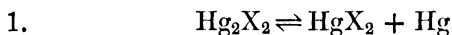
Thus we may say qualitatively that the ion  $Ag(CN)_2^-$  is more stable than the ion  $Ag(NH_3)_2^+$  (the ion formed when silver salts dissolve in ammonia), but that the former ion also yields minute quantities of silver ions.

In the case of very stable ions this is all the information the solubility method can give us.

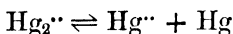
When the complex is less stable, however, a more complete knowledge of its properties can be arrived at by means of solubility measurements alone, and we shall now describe the methods by which such information may be gained.

A general method for the determination of the constitution of a complex ion from solubility measurements was

first given by Sherill (*Zeit. phys. Chem.*, **43**, 705 (1903)) and applied by him to the case of the mercury halides. In this case the following general relations hold, where X represents an atom of the halide :—



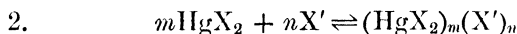
or in terms of the reacting ions



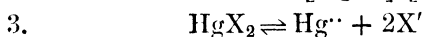
This equilibrium was observed by Richards (*Zeit. phys. Chem.*, **24**, 39 (1897)), and investigated by Abel (*Zeit. anorg. Chem.*, **26**, 361 (1901)), who showed that the mercurous ion has the formula  $\text{Hg}_2^{++}$ , and found the value of the constant

$$K = \frac{[\text{Hg}_2^{++}]}{[\text{Hg}^{++}]} = 120$$

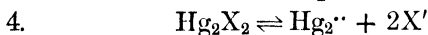
the concentration of the metallic mercury being constant.



$$K_1 = \frac{[(\text{HgX}_2)_m(\text{X}')_n]}{[\text{HgX}_2]^m[\text{X}']^n}$$



$$K_2 = \frac{[\text{Hg}^{++}][\text{X}']^2}{[\text{HgX}_2]}$$



$$K_3 = \frac{[\text{Hg}_2^{++}][\text{X}']^2}{[\text{Hg}_2\text{X}_2]}$$

If the mercurous salt is present in excess its concentration in the solution will be constant, and thus from (1) the concentration of undissociated mercuric halide is also constant. Thus the undissociated mercurous halide behaves like a less soluble modification of the mercuric halide which is in equilibrium with it.

From (2) we obtain

$$\frac{[(\text{HgX}_2)_m(\text{X}')_n]}{[\text{X}']^n} = K_1[\text{HgX}_2]^m = K_4$$

Since the amount of free mercuric halide present in an alkali halide solution (in which the experiments were

conducted) is very small, we may put the total content of mercuric halide in the solution equal to the mercuric mercury content of the complex. Compared with the total amount of mercury in the solution the solubility of the mercurous halide is also negligible, so that analytically the amount of mercury present as complex is given by the solubility of the mercurous salt. That no appreciable amount of mercurous complex ion is formed is shown by the fact that (analytically) the solution contains only mercuric halide.

Let  $a$  be the initial concentration of alkali halide,  $c$  the concentration of mercuric halide present as complex. In the present case we may put  $c$  equal to the concentration of mercurous salt dissolved.

We thus obtain the equation

$$K_4 = \frac{\frac{c}{m}}{\left(a - \frac{n}{m} \cdot c\right)^n}$$

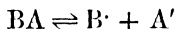
in which  $m$  and  $n$  are unknown integers and  $K$  is a constant of unknown value. For practical purposes we may assume complete dissociation of the alkali halide and of the complex salt.

We now proceed to find by trial values of  $m$  and  $n$  (whole numbers) which cause  $K_4$  in the above expression to remain constant while the concentration of the alkali halide (which determines the apparent solubility of the mercurous halide) is altered.

This method is based upon measurements of the solubility of the salt forming the "neutral part" in solutions of that providing the separate ion.

Another method of attacking the problem which is useful in cases where the neutral part is itself freely soluble is based upon measurements of the solubility of a sparingly soluble salt yielding the separate ion as a product of its dissociation. This gives us the concentration of the separate ion in any solution.

We may consider the case of a salt BA which dissociates according to the scheme



the extent of the dissociation being determined by the equation

$$K = \frac{[B'] [A']}{[BA]}$$

In saturated solution the product  $[B'] [A']$  is constant. We may call this L and the concentration of the undissociated part A. Then in any solution the concentration of the separate ion A is given by

$$[A'] = \frac{L}{\eta - A}$$

where  $\eta$  is the solubility of the salt BA in the solution.  $[A']$  here includes the ions provided by the salt BA itself.

L and A may be determined by measuring the conductivity of a saturated solution of the salt BA in water, or, if the solubility be very small, by indirect means.

A third method of attack by means of solubility consists, theoretically, in determining the solubility of the salt providing the "free ion" in solutions of that forming the neutral part. Up to the present this has not been employed, as it has generally been found convenient to use alkali salts for providing the free ion, and the solubility of these is usually too large to admit of mathematical treatment according to the simple law of mass action.

## CHAPTER VI

### THE ELECTRICAL POTENTIAL METHOD

THIS method consists in deducing the concentration of an ion in solution from measurements of the potential of an electrode which dips into it.

If a strip of a metal dips into a solution containing ions of the same metal a difference of potential is, in general, produced at the boundary between metal and liquid, so that the metal strip becomes either positively or negatively charged with respect to the solution. If the ion has the valency  $n$ , and we denote the charge per gram equivalent (96,540 coulombs) by  $F$ , and the difference in potential by  $E$ , the electrical work done by the system when one gram ion passes from the electrode is  $nFE$  joules, the sign depending upon the sign of the E.M.F. At the concentration of the solution let this gram ion occupy a volume  $v$  under the osmotic pressure  $p$ .

We may next allow this gram ion to expand to a volume  $v + dv$  under the corresponding pressure  $p - dp$ . The system thus yields the further quantity of work  $p dv$ , neglecting terms of the second order. Let the E.M.F. now be  $E + dE$ .

Finally, let our gram ion be re-deposited on the electrode, requiring the expenditure of the quantity of work  $nF(E + dE)$ , and leaving the system in its initial state.

Adding together the quantities of work yielded by the system (positive) and performed upon it (negative) we obtain

$$nFE + p dv - nF(E + dE) = 0$$

whence

$$nF dE = p dv$$

From the gas laws,

$$p dv = - v dp$$

and

$$v = \frac{RT}{p}$$

Hence

$$nF \cdot dE = -RT \cdot \frac{1}{p} dp$$

from which we obtain

$$nFE = -RT \log_e p + \text{a constant}$$

We may put this constant equal to  $RT \log P$ , where  $P$  is a constant having the dimensions of pressure. It is then evident that if  $p = P$ ,  $E = 0$ , and the system is in equilibrium.  $P$  is therefore called the electrolytic solution pressure for the metal under consideration. We thus obtain

$$E = - \frac{RT}{nF} \log_e p + \frac{RT}{nF} \log_e P$$

or

$$E = \frac{RT}{nF} \log_e \frac{P}{p}$$

$F$  being measured in coulombs and  $R$  in joules,  $E$  is given in volts by this expression.

The E.M.F. existing between a single electrode and a solution surrounding it is called an *electrode potential*.

The osmotic pressure,  $p$ , is proportional to the concentration of the ions, which we may call  $c$ . Thus we get the equation

$$E = e_0 - \frac{RT}{nF} \log_e c$$

If  $c$  be measured in gram ions per litre,  $e_0$  is the E.M.F. when the solution contains one gram ion per litre. This E.M.F. is called the *electrolytic potential* of the ion concerned.

This quantity has been determined for most of the elements. As is readily to be seen from the form of the expression,  $e_0$  can be calculated if we measure  $E$  for a solution in which the concentration of the ions is known.

Taking  $R = 8.315$  joules,  $F = 96,540$  coulombs, fixing

T at 25° C., *i.e.* 298° abs., and transforming the logarithm to the base 10, we obtain

$$E = e_0 - \frac{0.059}{n} \log_{10} c$$

Thus we see that at 25° C. the potential of a monovalent metal changes by 0.059 volt for every change of tenfold in the ionic concentration of the solution, and the potential of a divalent metal changes by 0.0295 volt under the same conditions.

Proportionate values for the change of E.M.F. may be calculated for other temperatures.

In the above calculation we have assumed that work is done by the system when the electrode dissolves, and hence that *E* increases as the solution becomes more dilute. This is true if we consider the ion to be a kation, and the potential that of the solution with respect to the electrode. Another system is in use in which the sign of the E.M.F. is reversed, and the potential is reckoned positive when the electrode is positive to the solution. In this case

$$E = e_0 + \frac{RT}{nF} \log_e c$$

In each case the sign must be reversed if the ion is an anion instead of a kation.

In a cell of the general type



in addition to the potential differences at the two boundaries between electrode and electrolyte there is generally a difference of potential between the two electrolytes, and in earlier investigations much difficulty was occasioned by the fact that in many cases this potential could not be determined.

The difference of potential across the liquid boundary between two electrolytes is entirely due to diffusion, since no chemical reaction is involved in the passage of the current. If we imagine a solution of hydrochloric acid in contact with water, both kinds of ion ( $H^+$  and  $Cl^-$ ) will diffuse from the acid solution into the water. As the



hydrogen ion tends to move faster than the chlorine ion, hydrogen ions will accumulate in the water in excess of the chlorine ions, giving the water a positive charge with respect to the acid. This will continue until the potential reaches a certain value, high enough to check further separation of the two ions, the system thus reaching a state of equilibrium.

It is easy to calculate the difference of potential which arises at the boundary of two solutions of the same binary electrolyte of different concentrations. Let the osmotic pressure due to each ion be  $p_1$  and  $p_2$  in the stronger and weaker solutions respectively, and let the transport number for the anion be  $x$ . If one faraday now passes through the solution from the stronger to the weaker portion, the osmotic work done upon the system is

$$x \cdot RT \log_e \frac{p_1}{p_2} - (1 - x)RT \log_e \frac{p_1}{p_2} = (2x - 1)RT \log_e \frac{p_1}{p_2}$$

Since the tendency of the ions to separate by diffusion is balanced by the E.M.F. produced, this expression is equal to the electrical work  $FE$ , and we find

$$E = (2x - 1) \frac{RT}{F} \log_e \frac{p_1}{p_2}$$

If we call the ionic mobilities for the anion and the kation  $u_A$  and  $u_K$  respectively

$$x = \frac{u_A}{u_A + u_K}$$

and hence

$$E = \frac{u_A - u_K}{u_A + u_K} \cdot \frac{RT}{F} \log_e \frac{p_1}{p_2}$$

If  $u_A = u_K$  the E.M.F. is nil; and the magnitude and sign of the potential depends upon the relative values of the ionic mobilities.

The above case—that of two solutions of the same binary electrolyte—is the simplest one. Equations applicable to more complex systems have been worked out by Planck (*Wied. Annalen*, **40**, 561 (1890)), K. R. Johnson (*Annalen der Physik*, **14**, 995 (1904)), Henderson (*Zeit. phys. Chem.*, **59**, 118 (1906); **63**, 325 (1908)), and Cumming (*Trans. Farad. Soc.*,

vol. 8, 1912). The equation of Planck and its extension by Johnson are excessively complicated, and in the case of polyvalent ions the practical solutions contain an element of uncertainty (Bjerrum, *Zeit. phys. Chem.*, **53**, 428 (1905)). Henderson's equation, however, is simpler, besides being based on premises which probably approximate more closely to practical conditions. It has been further simplified by Cumming for the case where the anion and kation of each salt has the same valency. These equations can be comparatively easily applied in practice, and give results which agree well with the values observed in control experiments, where the sum of the electrode potentials is known.

Several experimenters have endeavoured to find means to eliminate practically the diffusion potential in two-liquid cells. Tower (*Zeit. phys. Chem.*, **20**, 198 (1896)) studied the effect of interposing between the electrolytes a strong solution of a salt yielding ions whose mobilities were nearly equal to one another, such as potassium chloride. As an example we may quote the values obtained by him for the cell



which are contained in the following table. The calculated values for the diffusion E.M.F.'s are calculated by means of Planck's formula. In each case the acid solutions were 0.005 N. with respect to  $\text{Mn}(\text{NO}_3)_2$ . This small concentration was neglected in calculating the diffusion P.D.

v KCl (litres).	Calculated P.D. at boundary between KCl and		Total P.D. due to diffusion (calculated).	Total P.D. of cell, calculated.	P.D. observed.
	0.1 N. $\text{HNO}_3$	0.05 N. $\text{HNO}_3$			
1	-0.0125	0.0090	-0.0035	0.0311	0.033
2	-0.0169	0.0120	-0.0049	0.0297	0.031
4	-0.0222	0.0169	-0.0053	0.0293	0.030
8	-0.0282	0.0219	-0.0063	0.0283	0.028
16	-0.0352	0.0280	-0.0072	0.0274	0.027
32	-0.0430	0.0350	-0.0080	0.0266	0.025
64	-0.0516	0.0429	-0.0087	0.0258	0.024
128	-0.0607	0.0515	-0.0092	0.0254	0.023

The total E.M.F. of a similar cell containing no potassium chloride and with the acid solutions in contact with one another was 0.023 volt, the calculated value being 0.0225 volt. (This value is obtained by means of the ordinary formula for oxydation-reduction cells, which in this case takes the form

$$E = \frac{RT}{2F} \log_e \frac{[H^+]_2^4}{[H^+]_1^4}$$

bearing in mind that the concentration of  $Mn^{++}$  ions may be taken as equal in the two solutions.)

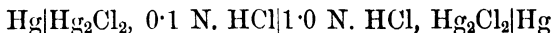
The total calculated electrode E.M.F. is 0.035 volt.

From these and similar results Tower concluded that the interposition of strong solutions of potassium chloride between different electrolytes has a certain tendency to diminish the diffusion potential, which disappears, however, as the solution is made more dilute.

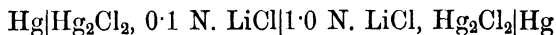
From this time onwards the method was generally used, but it possessed the disadvantage that in cases where the diffusion potential could not be calculated it was impossible to fix definite limits to the error caused by the small remaining P.D.

The problem was further studied by Bjerrum (*loc. cit.*), who extrapolated to find the potential due to the action at the electrodes alone, from measurements with saturated and half-saturated solutions of potassium chloride, on the assumption that the unremoved potential due to diffusion in the former case was half that in the latter. Very satisfactory agreement was found between the extrapolated values and those obtained by calculating the diffusion potentials without the insertion of a middle electrolyte and subtracting these from the values obtained by measurement under the same conditions. Bjerrum concluded that the error in the extrapolated values could only at the most be of the same order of magnitude as the difference between the potentials found experimentally, using saturated and half-saturated solutions of potassium chloride respectively.

A further great improvement was introduced by Cumming (*Trans. Faraday Soc.*, **2**, 213 (1907)), who found that in cells of the types



and



the diffusion E.M.F. was almost entirely removed by interposing a saturated solution of ammonium nitrate between the two electrolytes.

The cells were chosen so as to have large diffusion potentials, the kation moving much faster than the anion in the first case and much more slowly in the second. For the first cell the calculated electrode E.M.F. is 0.0563 volt. The mean experimental value for the E.M.F. of the cell was found to be 0.0950 volt. When saturated ammonium nitrate was interposed between the two hydrochloric acid solutions the E.M.F. was 0.0565 volt.

In the second case, the observed E.M.F. of the cell was 0.0361 volt, and the diffusion potential calculated from conductivity data was 0.0169 volt acting in the opposite direction to the electrode E.M.F. Adding together these values we obtain for the electrode E.M.F. the value 0.0530 volt; or calculating the electrode E.M.F. from Nernst's formula we find  $e = 0.0522$  volt. When a 10 N. solution of ammonium nitrate was interposed between the electrolytes the E.M.F. of the cell was found to be 0.0543 volt.

It is therefore probable that in general the diffusion potential between two electrolytes is nearly all removed by interposing a concentrated solution of ammonium nitrate between them. Since its introduction, this method of removing diffusion potentials has been extensively used.

The electrical potential method has been one of the most fruitful ones in the investigation of complex-formation. A general preliminary study of the behaviour of a number of salts from this point of view was made by Abegg and

Labendzinski (*Zeit. für Elektrochemie*, **10** (1904)), who measured the E.M.F.'s of cells of the type

Metal|Salt of metal|1.0 N. calomel electrode

using the nitrate, chloride, sulphate, and acetate of various metals. The potentials observed showed that at a given concentration the amounts of metal ions present varied enormously according to the character of the anion, and for the following series of anions continuously decreased:  $\text{NO}_3'$ ,  $\text{Cl}'$ ,  $\text{SO}_4''$ ,  $\text{C}_2\text{H}_3\text{O}_2'$ . Since conductivity measurements show that salts of all these anions are largely electrolytically dissociated, it follows that complex-formation must have occurred, causing the concentration of free metal ions to fall to very small values.

In order to find the constitution of a complex ion, it is not necessary to know the absolute concentrations of the components in the system. All we need is to find their rate of change with respect to one another, so as to be able to obtain the indices in an equation of the type

$$k = \frac{[\text{M}\cdot]^q [\text{A}']^r}{[\text{M}_q\text{A}_r]}$$

in which  $\text{M}\cdot$  represents a positively charged ion,  $\text{A}'$  a negatively charged one, and the complex ion  $\text{M}_q\text{A}_r$  has  $q-r$  positive charges (or  $r-q$  negative ones). A method of doing this was first given by Bodländer (*Festschrift zu Dedekind*, Braunschweig, 1901), and we shall now describe this.

Applying the above equation to two solutions of different concentrations, we obtain

$$\frac{[\text{M}\cdot]_1^q}{[\text{M}\cdot]_2^q} = \frac{[\text{M}_q\text{A}_r]_1}{[\text{M}_q\text{A}_r]_2} \cdot \frac{[\text{A}']_2^r}{[\text{A}']_1^r}$$

We now proceed to make  $[\text{A}']_1 = [\text{A}']_2$ . This can be achieved in practice by working with small concentrations of the metal M (and therefore of  $\text{M}\cdot$  and  $\text{M}_q\text{A}_r$ ) in presence of a large excess of another salt having  $\text{A}'$  as its anion. Under these conditions

$$\frac{[\text{M}\cdot]_1^q}{[\text{M}\cdot]_2^q} = \frac{[\text{M}_q\text{A}_r]_1}{[\text{M}_q\text{A}_r]_2}$$

If  $e$  be the electrode E.M.F. of the concentration cell  
 $M | \text{Solution I} || \text{Solution II} | M$

$$\begin{aligned} \text{we have } e &= \frac{RT}{nF} \log \frac{[M\cdot]_1}{[M\cdot]_2} \\ &= \frac{RT}{nF} \log \left( \frac{[M_q A_r]_1}{[M_q A_r]_2} \right)^{\frac{1}{q}} \end{aligned}$$

$$\text{whence } q = \frac{RT}{nFc} \log \frac{[M_q A_r]_1}{[M_q A_r]_2}$$

In cases where the complex ion is known to be stable, as, for example, in solutions of silver chloride in ammonia where the solubility is almost entirely due to complex formation, the complex-concentration  $[M_q A_r]$  ( $M$  in this case stands for the metal while  $A$  represents an ammonia molecule) may be written equal to the total concentration of the metal, without sensible error. We can thus solve the above equation for  $q$ .

Similarly we may find  $r$  by making the concentrations of the complex ion in the two solutions equal to one another. We then obtain the equation

$$\begin{aligned} \frac{[M\cdot]_1^q}{[M\cdot]_2^q} &= \frac{[A']_2^r}{[A']_1^r} \\ \text{Now } e &= \frac{RT}{nF} \log \frac{[M\cdot]_1}{[M\cdot]_2} \\ &= \frac{RT}{nF} \log \left( \frac{[A']_2}{[A']_1} \right)^{\frac{r}{q}} \end{aligned}$$

$$\text{Hence } \frac{r}{q} = \frac{e}{\frac{RT}{nF} \log \frac{[A']_2}{[A']_1}}$$

from which we find the value of  $r$ . We thus obtain the composition of the complex ion.

This theorem has been extended (Jaques, *Trans. Faraday Soc.*, 5, 225 (1910)) to the case in which the concentrations of the complex ion in the two solutions are not equal. In this case, as before

$$\frac{[M\cdot]_1^q}{[M\cdot]_2^q} = \frac{[M_q A_r]_1}{[M_q A_r]_2} \cdot \frac{[A']_2^r}{[A']_1^r}$$

$$\begin{aligned}
 \text{We now have } e &= \frac{RT}{nF} \log \frac{[M\cdot]_1}{[M\cdot]_2} \\
 &= \frac{RT}{nF} \log \left( \frac{[M_q A_r]_1}{[M_q A_r]_2} \right)^{\frac{1}{q}} \left( \frac{[A']_2}{[A']_1} \right)^{\frac{r}{q}} \\
 &= \frac{1}{q} \cdot \frac{RT}{nF} \left( \log \frac{[M_q A_r]_1}{[M_q A_r]_2} + r \log \frac{[A']_2}{[A']_1} \right)
 \end{aligned}$$

$$\text{Thus } \frac{r}{q} \cdot \frac{RT}{nF} \log \frac{[A']_2}{[A']_1} = e - \frac{1}{q} \cdot \frac{RT}{nF} \log \frac{[M_q A_r]_1}{[M_q A_r]_2}$$

whence, putting  $[M_q A_r]_1$  and  $[M_q A_r]_2$  equal to  $C_1$  and  $C_2$  respectively, we obtain

$$r = \frac{qe + \frac{RT}{nF} \log \frac{C_2}{C_1}}{\frac{RT}{nF} \log \frac{[A']_2}{[A']_1}}$$

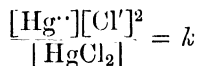
This equation can in general be solved, remembering that  $q$  and  $r$  are necessarily integers (cf. Appendix 2).

## CHAPTER VII

### SOME EXAMPLES

As an example of the application of the methods developed in the two preceding chapters, we may consider the case of the mercuric halide complexes.

As early as 1842 Miahle (*Ann. Chim. Phys.*) observed that mercuric chloride was much more soluble in solutions of chlorides than in water. According to our present theory this is a sure indication of the formation of a complex ion. Under normal circumstances the solubility would be depressed by the presence of chlorine ions, and any excess of solubility over that calculated from the law of mass action must be caused by a portion of the salt having been removed from direct equilibrium with the chlorine and mercury ions, as explained in Chapter V. The ionisation of mercuric chloride is actually very slight, so that the calculated solubility in a chloride solution would be very little different from the value in water. The equation for equilibrium,



must hold good, however, and the excess of mercuric chloride must, therefore, be regarded as having ceased to function as a component in this system.

Le Blanc and Noyes (*Zeit. phys. Chem.*, **6**, 401 (1890)) studied the problem of determining the constitution of such solutions by means of cryoscopic measurements. These afford still another method of investigating the formation of complex ions. Since the depression of the freezing point of



a solvent is proportional to the number of molecules per unit volume (for dilute solutions) that it contains, we can find out whether two substances form a compound in solution by measuring the freezing point of the mixed solution, and, if the combination is practically complete, in what proportions the substances combine with one another.

Le Blanc and Noyes determined the freezing points of solutions of hydrochloric acid in which various amounts of mercuric chloride were dissolved. The following table shows the results obtained by them for 1.0 N. hydrochloric acid :—

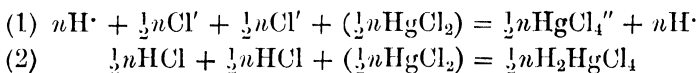
Conc. of $\text{HgCl}_2$ mols. per litre.	Freezing point.	Difference.
0	-3.965	—
1	-3.785	0.180
2	-3.560	0.225
3	-3.435	0.125
4	-3.350	0.085
5	-3.380	-0.030
6	-3.395	-0.015
7	-3.425	-0.030

The fact that on adding small quantities of mercuric chloride to the solution the freezing point rises, shows definitely that a diminution in the number of molecules in the solution has occurred. From the above results and those obtained at other concentrations of hydrochloric acid it was found that the maximum in the freezing point occurs when half a molecule of mercuric chloride is present for each molecule of hydrochloric acid.

If one molecule of hydrochloric acid attached itself to one molecule of mercuric chloride, and the reaction were complete, the freezing point would remain unchanged. It follows that at least two molecules of hydrochloric acid must combine with a molecule of mercuric chloride, unless we suppose that the rise in the freezing point is caused by the (monobasic) complex acid having a very much smaller degree of dissociation than hydrochloric acid. Special experiments were made to settle this point.

From a knowledge of the freezing point and the electrical conductivity of mercuric chloride solutions alone it was evidently impossible that the degree of dissociation of free hydrochloric acid could be appreciably affected by the very small concentration of chlorine ions produced by the mercuric chloride.

Turning our attention to the case where two molecules of hydrochloric acid combine with one of mercuric chloride, we obtain the following scheme for the reaction between (1) the dissociated molecules and (2) the undissociated molecules, assuming that the ionised hydrochloric acid yields ionised complex acid, and that the unionised hydrochloric acid yields unionised complex acid:—



We thus find that, compared with the original solution of hydrochloric acid of concentration  $n$  molecules per litre, the complex solution contains  $\frac{1}{2}n$  molecules per litre less. For a normal solution of hydrochloric acid the maximum rise in the freezing point that could be caused by addition of mercuric chloride should therefore be half the molecular depression of the freezing point for water, viz.  $\frac{1.89^\circ}{2} = 0.95^\circ$ .

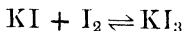
The maximum rise actually found was  $0.62$ , so that if the acid  $\text{H}_2\text{HgCl}_4$  is formed, its formation must be incomplete. This hypothesis is borne out by the fact that in weaker solutions of hydrochloric acid the rise in the freezing point is proportionately less, as would follow from the law of mass action.

If compounds containing more than two molecules of hydrochloric acid to one of mercuric chloride are formed, these must be still more dissociated into their constituent molecules, and a simple calculation shows that under these circumstances the concentration of free mercuric chloride would reach the limit of its solubility before the solution actually ceases to dissolve the salt.

We are therefore obliged to conclude that either (1) the compound  $\text{H}_2\text{HgCl}_4$  is formed but shows a considerable dissociation into  $\text{HCl}$  and  $\text{HgCl}_2$  (electrolytically it cannot be much more dissociated than hydrochloric acid), or (2) that the compound  $\text{HHgCl}_3$  is formed and is much less electrolytically dissociated than  $\text{HCl}$ .

In order to decide this point measurements were made of the speed of catalysis of methyl acetate by the complex solution, and it was found that the rate was practically independent of the presence of mercuric chloride. Thus the complex acid must be highly dissociated, and we conclude that the compound  $\text{H}_2\text{HgCl}_4$  is formed and is a strong acid, dissociating to about the same extent as hydrochloric acid, and yielding the complex ion  $\text{HgCl}_4^{--}$ .

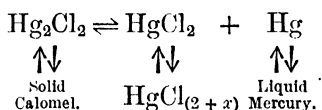
The same authors studied solutions of iodine in potassium iodide solutions in a similar manner, and found that addition of iodine to potassium iodide caused a slight rise in the freezing point instead of the very considerable lowering that would be produced if no combination had occurred. Constancy of the freezing point would indicate the formation of the compound  $\text{KI}_3$ , according to the scheme



We thus obtain additional evidence for the existence of this complex compound, accompanied probably by small quantities of higher iodides, in exact agreement with the results of Roloff and of Jakowkin, which were given in Chapter IV.

Returning to the subject of the mercuric halide complexes, Richards (*Zeit. phys. Chem.*, **24**, 39 (1897)), in the course of an investigation of the temperature coefficient of the E.M.F. of the calomel electrode, observed that the calomel was noticeably decomposed into mercuric chloride and mercury in presence of other chlorides, and ascribed the apparent acceleration of the reaction by chlorides to a "catalytic" effect. Later (*Zeit. phys. Chem.*, **40**, 385 (1902)) Richards and Archibald studied the action of various chloride solutions upon calomel, and found that the system reached

a definite equilibrium-point. The amount of mercuric chloride in the solution increased with increase of the chloride concentration, and this increase was roughly proportional to the square of the concentration of chlorine ions in the solution. We may represent the system by the scheme



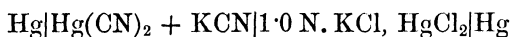
from which we see that of the three substances entering into the reaction, the concentrations of two (calomel and mercury) are fixed. The concentration of the third component is therefore also fixed, that is, the concentration of  $\text{HgCl}_2$ -molecules must have a constant value if the solution is in contact with solid calomel and liquid mercury. The excess of mercuric chloride must therefore be present as some other compound, and since this is conditioned by the presence of chlorine ions it must be in the form of either (1) a complex ion of the type  $\text{HgCl}_{(2+x)}'$ , or (2) the corresponding undissociated double salt. As already pointed out in Chapter V, the amount of mercury in an aqueous solution of calomel, including the mercuric chloride produced, may be neglected in comparison with the total content of a saturated solution containing alkali chloride, and we may therefore take the total mercury content of the solution as being present as complex ion. This should be proportional to the  $x$ th power of the chlorine ion concentration, since

$$[\text{HgCl}_2][\text{Cl}]^x = k \cdot [\text{HgCl}_{(2+x)}]$$

$x$  must therefore be approximately 2, or, in other words, the complex  $\text{HgCl}_4''$  is formed in larger quantities than any others.

The formation of complex ions in solutions of mercuric cyanide, chloride, bromide, and iodide was exhaustively studied by Sherill (*Zeit. phys. Chem.*, **43**, 705 (1903)), who first developed the scheme for the measurement of the dissociation constant of a complex ion by means of solubility

measurements given in Chapter V. Sherill measured the potential of the cell



using various concentrations of mercuric cyanide and potassium cyanide respectively. No precautions were taken to estimate or eliminate diffusion potential. This would probably be small, however, as the molecular conductivity of potassium cyanide does not differ much from that of potassium chloride, so that the mobility of the cyanogen ion must be nearly the same as that of the chlorine ion. The accompanying table shows the values that were found:—

No.	Conc. KCN.	Conc. $\text{Hg}(\text{CN})_2$	E.M.F. against N. E. volts.	E.M.F. against No. 1 volts.	E.M.F. against No. 1 calculated from formula $\text{Hg}(\text{CN})_2(\text{CN})_2''$ volts.	Conc. of $\text{Hg}^{++}$ .	$K = \frac{[\text{Hg}(\text{CN})_2(\text{CN})_2'']}{[\text{Hg}^{++}][\text{CN}]^4}$
1	0.049	0.01247	0.519	—	—	$1.3 \cdot 10^{-37}$	$2.8 \cdot 10^{11}$
2	0.0983	0.01247	0.575	0.056	0.057	$1.7 \cdot 10^{-39}$	$2.5 \cdot 10^{11}$
3	0.0983	0.02493	0.547	0.028	0.027	$1.7 \cdot 10^{-38}$	$2.7 \cdot 10^{11}$
4	0.1965	0.01247	0.616	0.097	0.102	$0.7 \cdot 10^{-40}$	$2.1 \cdot 10^{11}$
5	0.1965	0.02493	0.600	0.081	0.084	$2.5 \cdot 10^{-40}$	$2.2 \cdot 10^{11}$
6	0.1965	0.04985	0.574	0.055	0.054	$1.8 \cdot 10^{-39}$	$3.2 \cdot 10^{11}$

Mean =  $2.5 \cdot 10^{11}$

In order to calculate the concentration of  $\text{Hg}^{++}$  ions, the concentration of these in the normal calomel electrode was taken as  $5.3 \times 10^{-20}$  gram ions per litre. The method by which this value was arrived at will be given in a later chapter (see Chapter X). Difficulty was experienced in making the measurements, as the E.M.F.'s did not remain perfectly constant.

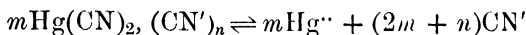
Applying the Bodländer method to the results we obtain  $r = 4$ , but the value of  $q$  is less than the minimum of 1. From the constancy of the values in the last column, however, it is evident that the main quantity of complex ions present must have the formula  $\text{Hg}(\text{CN})_4''$ .

The solutions used in these experiments all contained a

considerable excess of potassium cyanide. In order to see whether complex ions containing less cyanogen would be formed under different circumstances, a method was worked out by which this information could be obtained from potential measurements with solutions saturated with mercuric cyanide.

In this case we have an additional unknown quantity to deal with, namely, the concentration of the cyanogen ions. This can be obtained at the expense of one of the indices in the equation for equilibrium.

We shall consider the dissociation of the complex according to the following scheme:—



whence 
$$\frac{[\text{Hg}_m(\text{CN})_{2m+n}]}{[\text{Hg}^{\cdot\cdot}]^m [\text{CN}']^{2m+n}} = K$$

Let  $a$  be the concentration of the alkali cyanide. Then the concentration of the complex  $\text{Hg}_m(\text{CN})_{2m+n}$  is given by  $\frac{a}{n}$ . Thus

$$K = \frac{\frac{a}{n}}{[\text{Hg}^{\cdot\cdot}]^m [\text{CN}']^{2m+n}}$$

Considering two solutions we obtain

$$\frac{a_1}{a_2} = \frac{[\text{Hg}^{\cdot\cdot}]_1^m [\text{CN}']_1^{2m+n}}{[\text{Hg}^{\cdot\cdot}]_2^m [\text{CN}']_2^{2m+n}}$$

Since the solutions are saturated with respect to  $\text{Hg}(\text{CN})_2$ , the solubility product  $[\text{Hg}^{\cdot\cdot}][\text{CN}']^2$  is a constant, and therefore

$$\frac{[\text{Hg}^{\cdot\cdot}]_1}{[\text{Hg}^{\cdot\cdot}]_2} = \frac{[\text{CN}']_2^2}{[\text{CN}']_1^2}$$

Hence

$$\frac{a_1}{a_2} = \frac{[\text{Hg}^{\cdot\cdot}]_1^m [\text{Hg}^{\cdot\cdot}]_2^{\frac{2m+n}{2}}}{[\text{Hg}^{\cdot\cdot}]^m [\text{Hg}^{\cdot\cdot}]_1^{\frac{2m+n}{2}}}$$

and

$$\left(\frac{a_2}{a_1}\right)^{\frac{2}{n}} = \frac{[\text{Hg}^{\cdot\cdot}]_1}{[\text{Hg}^{\cdot\cdot}]_2}$$

The E.M.F. of the concentration cell containing the two solutions is

$$E = 0.0295 \log \frac{[\text{Hg}^{++}]_1}{[\text{Hg}^{++}]_2}$$

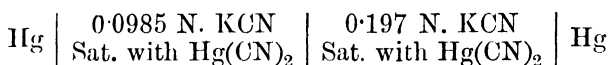
Substituting from the previous equation we get

$$n = \frac{0.059}{E} \log \frac{a_2}{a_1}$$

or 
$$E = \frac{0.059}{n} \log \frac{a_2}{a_1}$$

We can thus find  $n$ , but not  $m$ .

The E.M.F. of the cell



was found to be 0.016 volt. Putting  $n=1$  and calculating the E.M.F., we find  $E = 0.017$ ; or, calculating  $n$ , we get  $n = 1.05$ .

It thus appears that when  $\text{Hg(CN)}_2$  is in excess the complex ion  $\text{Hg(CN)}_3^-$  is formed at the expense of the ion  $\text{Hg(CN)}_4^{2-}$ .

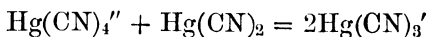
The cryoscopic method was next applied, the effect of the addition of  $\text{Hg(CN)}_2$  to solutions of KCN upon the freezing point being observed. The following table shows the results obtained:—

Conc. KCN.	Total conc. $\text{Hg(CN)}_2$ .	Increase in conc. of $\text{Hg(CN)}_2$ .	Freezing point.	Rise in freezing point.	Rise $\div 1.85$ = diminution in gram mols. per litre.
0.1965	0.00	—	—0.704	—	—
0.1965	0.0476	0.0476	—0.608	0.096	0.052
0.1965	0.0953	0.0476	—0.534	0.074	0.04
0.1965	0.1905	0.095	—0.678	—0.144	—0.078
0.1965	0.3910	0.191	—0.990	—0.312	—0.168
0.50	0.00	—	—1.745	—	—
0.50	0.21	0.21	—1.280	0.465	0.25
0.50	0.30	0.09	—1.296	—0.016	—0.009
0.50	0.36	0.06	—1.410	—0.114	—0.062
0.50	0.42	0.06	—1.507	—0.097	—0.052
0.50	0.50	0.08	—1.653	—0.146	—0.079

From these values we may draw the following conclusions:—

During the addition of  $\text{Hg}(\text{CN})_2$  to the solution, for each molecule of  $\text{Hg}(\text{CN})_2$  added the solution contains one molecule *less*, that is, *two*  $\text{CN}'$  ions must disappear for each  $\text{Hg}(\text{CN})_2$  molecule added. This continues until the solution contains half a molecule of added mercuric cyanide for each molecule of potassium cyanide. From this point onwards addition of  $\text{Hg}(\text{CN})_2$  causes a lowering of the freezing point corresponding to an increase in the number of molecules per litre which is equal to the number of molecules of  $\text{Hg}(\text{CN})_2$  added.

This latter behaviour may be the outcome of either or both of two states of affairs in the solution. Either (1) the added  $\text{Hg}(\text{CN})_2$  remains unchanged or (2) it reacts with the  $\text{Hg}(\text{CN})_4''$  ions already present according to the scheme



From the results obtained from the potential measurements it will be seen that the latter process must be regarded as occurring to a considerable extent at least. This point was further investigated by determining the solubility of  $\text{Hg}(\text{CN})_2$  in KCN solutions.

If the first state of affairs mentioned above were that actually existing, the only reaction occurring would be that represented by the equation



The *increase* in solubility of the mercuric cyanide should therefore be equal to half the concentration of the potassium cyanide. On the other hand, if the solution behaves according to the second scheme, the increase in the solubility of the mercuric cyanide must be greater than half the concentration of the KCN; and if the formation of the complex  $\text{Hg}(\text{CN})_3'$  were complete in the saturated solution, the increase in the solubility would be equal to the concentration of KCN.

The solubility of  $\text{Hg}(\text{CN})_2$  in water was found to be 0.44 gram molecule per litre at 25°. The following table shows



the solubility in three solutions of KCN and the increase over the solubility in water:—

Conc. KCN.	Solubility of $\text{Hg}(\text{CN})_2$ .	Increase in solubility.
0.00	0.44	—
0.0493	0.4855	0.0455
0.0985	0.5350	0.095
0.1970	0.627	0.187

Since the increase in solubility is actually nearly equal to the concentration of KCN, it follows that the formation of the complex ion  $\text{Hg}(\text{CN})_3'$  in solutions saturated with  $\text{Hg}(\text{CN})_2$  is nearly complete. Since the dissociation of mercuric cyanide in solution is exceedingly small, the depression of solubility caused by the potassium cyanide is quite negligible.

On account of the high stability of the complex  $\text{Hg}(\text{CN})_3'$ , it is not possible to examine its dissociation by any method except that of potential measurements. Its formation in strong solutions of  $\text{Hg}(\text{CN})_2$  in KCN, however, was further investigated by means of distribution measurements.

Aqueous solutions of potassium cyanide containing  $\text{Hg}(\text{CN})_2$  were shaken with ether, and the distribution ratio of the  $\text{Hg}(\text{CN})_2$  between the two liquids was determined. The accompanying table shows the values found:—

Conc. KCN.	Conc. $\text{Hg}(\text{CN})_2$ in aqueous layer.	Free $\text{Hg}(\text{CN})_2$ in aqueous layer.	Conc. $\text{Hg}(\text{CN})_2$ in ether.	Distribution coefficient.
0.00	0.44	0.44	0.01	44
0.0493	0.410	0.361	0.00785	46
0.0493	0.370	0.321	0.00685	47
0.0493	0.300 <sup>1</sup>	0.251	0.00567	44
0.0493	0.274	0.225	0.00413	44

The concentration of free  $\text{Hg}(\text{CN})_2$  in the aqueous layer was obtained by subtracting the concentration of KCN from that of the total  $\text{Hg}(\text{CN})_2$ , that is, by assuming the complete formation of the complex ion  $\text{Hg}(\text{CN})_3'$ .

<sup>1</sup> Given as 0.200 in the original.

The fact that the distribution coefficient calculated in this way remains constant and has the same value as that obtained for the saturated solution in absence of KCN affords strong evidence in corroboration of that obtained in the previous experiments for the formation of the complex ion  $\text{Hg}(\text{CN})_3'$ . It must be added, however, that this set of experiments, taken alone, would have carried more weight if determinations of the distribution coefficient had been made in absence of KCN over the range of concentrations given for the free  $\text{Hg}(\text{CN})_2$  in order to gain assurance that the coefficient really is independent of the concentration.

Experiments similar to the above were carried out with solutions of  $\text{HgI}_2$ ,  $\text{HgBr}_2$ , and  $\text{HgCl}_2$  in solutions of the corresponding alkali halides. In the case of these salts, a saturated solution in contact with mercury cannot exist, as the corresponding mercurous compound is precipitated, and the E.M.F. measurements could not therefore be extended to these. A long series of E.M.F. measurements showed that in solutions which did not contain a great excess of KI, a complex was formed which contained less than two added iodine ions. Distribution experiments by Dawson (*Trans. Chem. Soc.*, **95**, 870 (1909)) also led to this result. In each case Sherill concluded that a complex ion of the type  $\text{HgX}_4''$  was mainly formed, but Sand and Breest (*Zeit. phys. Chem.*, **59**, 424 (1907)) have shown that Sherill's distribution experiments in the cases of mercuric bromide and chloride can be better interpreted by assuming the formation of the ion  $\text{HgX}_3'$ .

One other set of Sherill's measurements may be mentioned as noteworthy. These depended upon the rate of catalysis of the decomposition of hydrogen peroxide by iodine ions, which had previously been measured by Bredig and Walton (*Zeit. Elektrochem.*, **9**, 114 (1903)). Bredig and Walton showed that the speed of decomposition was proportional to the concentration of iodine ions. By observing the speed of decomposition induced by the complex solution, the concentration of the iodine ions in it could be determined.

On subtracting this from the total concentration of potassium iodide in the solution (assuming complete dissociation) we find the concentration of iodine ions present as complex, and since

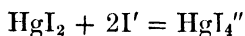
$$m\text{HgI}_2 + n\text{I}' = (\text{HgI}_2)_m\text{I}_n'$$

on dividing the concentration of "bound" iodine ions by the concentration of  $\text{HgI}_2$  we obtain the ratio  $\frac{n}{m}$ . The following table shows the results obtained:—

Conc. KI.	Conc. $\text{HgI}_2$ .	K = velocity constant.	Conc. $\text{I}'$ .	Conc. "bound" $\text{I}'$	Conc. "bound" $\text{I}'$ Conc. $\text{HgI}_2$ $= \frac{n}{m}$
0.03125	0.00	0.04145	0.03125	0.00	—
"	0.00205	0.03639	0.0274	0.0039	1.9
"	0.00397	0.03241	0.0244	0.0069	1.74
"	0.00547	0.0286	0.0215	0.0097	1.77
"	0.00798	0.02326	0.0176	0.0136	1.70
"	0.01017	0.01856	0.01395	0.0173	1.70
"	0.01078	0.01775	0.0134	0.0178	1.65
"	0.01161	0.01665	0.01255	0.0187	1.61
"	0.01315	0.01453	0.01094	0.0203	1.54

Thus it appears that while in solutions that are weak with respect to  $\text{HgI}_2$ , such as were used for the E.M.F. measurements,  $\frac{n}{m}$  is practically 2, the value of this ratio continually falls as the amount of  $\text{HgI}_2$  in solution increases. Another similar set of measurements made with solutions of various concentrations of KI, and saturated with respect to  $\text{HgI}_2$  gave values of  $\frac{n}{m}$  ranging from 1.63 in 0.23 N. KI to 1.50 in 0.018 N. KI.

Freezing-point experiments showed that for every molecule of  $\text{HgI}_2$  introduced, the total number of molecules in solution was diminished by one. This can only be explained by assuming the formation of  $\text{HgI}_4''$  according to the equation

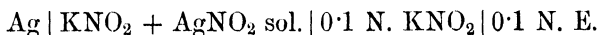


and not, as Sherill supposed, by the formation of a complex of the general type  $(\text{HgI}_2)_x(\text{I}')_{x+1}$ , which would only cause the concentration to fall by one gram molecule per litre for the addition of  $x$  gram molecules of  $\text{HgI}_2$ . Sherill's assumption of the formation of the complex ion  $(\text{HgI}_2)_2\text{I}_3'''$  is therefore based upon an error so far as freezing-point experiments are concerned. The evidence for the formation of this compound must be regarded as very slight, since another interpretation can be placed upon the experiments on the catalysis of the decomposition of hydrogen peroxide and Dawson's results, namely, the partial formation of the ion  $\text{HgI}_3'$ .

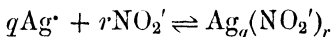
The existence of the complex ions  $\text{HgBr}_4''$  and  $\text{HgCl}_4''$  was shown in a manner similar to the above.<sup>1</sup>

In illustration of the direct solubility method of attacking these problems, which in Sherill's work did not give simple results, we may quote the results of an investigation by Pick (*Dissert.*, Breslau, 1906: *Zeit. anorg. Chem.*, **51**, 1 (1906)) of solutions of silver nitrite.

Measurements of the E.M.F. of the cell



showed that in the scheme



$q = 1$  and  $r = 2$ , and a very concordant set of values was calculated for the constant

$$k_1 = \frac{[\text{Ag}^*][\text{NO}_2']^2}{[\text{Ag}(\text{NO}_2)_2']}$$

using the known electrolytic potential of silver. These gave the mean value of  $k_1$  as  $1.47 \times 10^{-3}$ .

These results were checked by means of solubility measurements, and the constant

$$k_2 = \frac{[\text{Ag}_m(\text{NO}_2)_{m+n}]}{[\text{AgNO}_2]^m[\text{NO}_2']^n}$$

was calculated on the assumption that  $m = 1$  and  $n = 1$ .

<sup>1</sup> But see Sand and Breest (*loc. cit.*).

Following the method of Sherill, we see that in saturated solutions the concentration  $[\text{AgNO}_2]$  ( $= b$ ) is constant, whence

$$\frac{[\text{Ag}_m(\text{NO}_2)_{m+n}]}{[\text{NO}_2']^n} = k_2 \times b^m = k_2'$$

If the total silver content of the solution be determined and have the value  $x$ , then

$$x - b - [\text{Ag}'] = c$$

$c$  being the concentration of silver atoms present as complex, corresponding to the complex concentration  $\frac{c}{m}$ . The solubility product of silver nitrite had been determined previously, and found to have the value  $2.0 \times 10^{-4}$  at  $25^\circ$ . Calculating the silver ion concentrations in the solutions used (see table), we find that the term  $[\text{Ag}']$  may be neglected in the above equation, so that we may write, with a sufficiently good approximation to the truth,

$$x - b = c$$

The concentration of nitrite ions contained in the form of complex is  $\frac{n}{m} \cdot c$ . Hence, if  $a$  be the initial concentration of  $\text{NO}_2$ -ions, we get when the system is in equilibrium

$$a - \frac{n}{m} \cdot c = [\text{NO}_2']$$

$$\text{Hence} \quad k_2' = \frac{c}{\left(a - \frac{n}{m} \cdot c\right)^n}$$

$a - c$  is given by subtracting twice the total silver concentration, less  $b$ , from the total nitrite ion concentration, on the assumption that  $m = n = 1$ , and again neglecting the presence of silver ions. As  $b$  is always very small compared with  $a - c$  in the solutions used, Pick neglected it also. This quantity,  $a - c$ , representing the total nitrite ion content, does not take account of the undissociated added

salt, and must accordingly be multiplied by  $a$ , its degree of dissociation.

The solubility of silver nitrite was accordingly determined in barium nitrite solutions, the values of  $a$  being taken from the conductivity measurements of Vogel (*Zeit. anorg. Chem.*, **35**, 407 (1903)).

The nitrite content of the solutions was determined by titration with potassium permanganate, and the silver concentration by Volhard's method. The results are given in the following table:—

Titration concentrations.		$\text{NO}_2 - 2\text{Ag}$ $= a - c.$	$\frac{[\text{NO}_2']}{= (a - c)a}.$	$\text{Ag} - b = c.$	$k_2' = \frac{c}{(a - c)a}$
$\text{NO}_2.$	$\text{Ag}.$				
0.9921	0.0625	0.8761	0.525	0.0508	0.097
0.8609	0.0554	0.7501	0.473	0.0437	0.092
0.8100	0.0495	0.7020	0.449	0.0378	0.084
0.5822	0.0379	0.5064	0.355	0.0262	0.074
0.4876	0.0327	0.4222	0.310	0.0210	0.068
0.3089	0.0239	0.2611	0.209	0.0122	0.058
0.2020	0.0202	0.1616	0.132	0.0085	0.064
0.1134	0.0173	0.0788	0.0678	0.0056	0.083

Mean = 0.077

It cannot be said that the constant exhibits a very high degree of constancy, but it may fairly be claimed that it is much more constant for  $m = n = 1$  than for any other values of these two coefficients; and it is to be remembered that a large number of experimental data is used in the calculation.

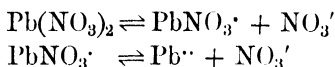
Few cases have been investigated in which the solubility and dissociation of the "neutral part" are such that the free ions produced by the dissociation cannot be neglected, and which thus require rigorous mathematical treatment based upon the principles given in Chapter V.

W. K. Lewis (*Dissert.*, Breslau, 1908) worked out the case of the nitrates of lead and potassium, each of which shows a greatly increased solubility in presence of the other. The

results appear to indicate the formation of a complex kation of the formula  $\text{KPbNO}_3^+$ ; or, at least, as Lewis says, "can be interpreted qualitatively and quantitatively within the limits of experimental error" by assuming the existence of this ion. The main evidence for the presence of potassium in the ion is the fact that sodium nitrate behaves normally with lead nitrate, that is, the two salts exert a mutually depressing influence upon their respective solubilities.

Unfortunately the saturated solutions of these salts are so concentrated that the law of mass action cannot be regarded as applying at all in a quantitative sense, and the mathematical investigation was confined mainly to measurements of electrode potentials in weaker solutions. The theoretical treatment of these measurements may be noticed.

We may assume that lead nitrate dissociates in two stages according to the scheme



The extent of the dissociation at each stage is therefore determined by the equations

$$K_1 = \frac{[\text{PbNO}_3^+][\text{NO}_3^-]}{[\text{Pb}(\text{NO}_3)_2]} \quad . \quad . \quad . \quad . \quad (1)$$

$$K_2 = \frac{[\text{Pb}^{++}][\text{NO}_3^-]}{[\text{PbNO}_3^+]} \quad . \quad . \quad . \quad . \quad (2)$$

In any solution, whether containing added alkaline nitrate or no, the total concentration of lead nitrate,  $c$ , is given by

$$c = [\text{Pb}^{++}] + [\text{PbNO}_3^+] + [(\text{PbNO}_3)_2] \quad . \quad . \quad (3)$$

In a pure solution of lead nitrate we have, further, since the solution is electrostatically neutral, the relation

$$2[\text{Pb}^{++}] + [\text{PbNO}_3^+] = [\text{NO}_3^-] \quad . \quad . \quad . \quad (4)$$

From (2) and (4) by elimination of  $[\text{PbNO}_3^+]$  we obtain

$$[\text{NO}_3^-] = \frac{2[\text{Pb}^{++}]K_2}{K_2 - [\text{Pb}^{++}]} \quad . \quad . \quad . \quad . \quad (5)$$

From (3) and (4) we may find  $[\text{Pb}(\text{NO}_3)_2]$  in terms of  $c$ ,  $[\text{Pb}^{\bullet\bullet}]$  and  $[\text{NO}_3']$ , and obtain

$$[\text{Pb}(\text{NO}_3)_2] = c - [\text{NO}_3'] + [\text{Pb}^{\bullet\bullet}]$$

Multiplying equations (1) and (2) together and substituting for  $[\text{Pb}(\text{NO}_3)_2]$ , we find

$$K_1 K_2 = \frac{[\text{Pb}^{\bullet\bullet}][\text{NO}_3']^2}{c - [\text{NO}_3'] + [\text{Pb}^{\bullet\bullet}]}$$

Substituting for  $[\text{NO}_3']$ , we get

$$K_1 K_2 = \frac{[\text{Pb}^{\bullet\bullet}] \left( \frac{2[\text{Pb}^{\bullet\bullet}] K_2}{K_2 - [\text{Pb}^{\bullet\bullet}]} \right)^2}{c - \frac{2[\text{Pb}^{\bullet\bullet}] K_2}{K_2 - [\text{Pb}^{\bullet\bullet}]} + [\text{Pb}^{\bullet\bullet}]}$$

which reduces to the quadratic equation in  $K_2$

$$K_2^2(c - [\text{Pb}^{\bullet\bullet}]) - K_2 \left( c + \frac{2[\text{Pb}^{\bullet\bullet}]^2}{K_1} \right) 2[\text{Pb}^{\bullet\bullet}] + [\text{Pb}^{\bullet\bullet}]^2(c + [\text{Pb}^{\bullet\bullet}]) = 0 \quad . \quad . \quad . \quad . \quad (6)$$

It can be shown by trial that  $\frac{2[\text{Pb}^{\bullet\bullet}]^2}{K_1}$  is small enough

to be neglected in comparison with  $c$ , and we thus obtain an equation giving  $K_2$  in terms of  $c$  and  $[\text{Pb}^{\bullet\bullet}]$ , which is likely to prove of value in future investigations of ternary electrolytes.

If we have two solutions of lead nitrate and find the ratio of the concentrations of lead ions in them by means of potential measurements, then obviously we are in a position to find  $K_2$  by trial, remembering that  $K_2$  is a constant. This method was used by Jaques (*loc. cit.*) in investigating the equilibria in solutions of lead acetate and cadmium acetate in alkali acetates. Lewis proceeded to make further approximations in the above equation (which we may refer to as "Lewis's equation"), and combined it with the Nernst equation

$$e = 0.0295 \log \frac{[\text{Pb}^{\bullet\bullet}]_1}{[\text{Pb}^{\bullet\bullet}]_2}$$

so as to obtain a direct solution. For details of these further calculations the reader should consult the original paper.



A provisional value of  $K_2$  was thus found. The following table reproduces Lewis's results,  $[Pb^{..}]$  in 0.01 molar solution being taken as 0.0087:—

$c$ .	$K_2$ .
0.01	0.128
0.05	0.088
0.25	0.103
0.4	0.108
1.0	0.126

In the case of a solution containing added alkaline nitrate, equation (4) no longer holds. From equations (1), (2), and (3) we obtain by elimination of  $[PbNO_3^+]$  and  $[Pb(NO_3)_2]$

$$[Pb^{..}] = \frac{K_1 K_2 c}{[NO_3^-]^2 + K_1 K_2 + K_1 [NO_3^-]} \quad (7)$$

This equation should hold for both the pure solution of lead nitrate and solutions containing alkaline nitrate.

Inserting the value found for  $K_2$  in the above equation, and using equation (5) in the case of pure lead nitrate solutions, we can now find the value of  $K_1$ . Lewis gives the following table of values obtained in this way:—

$c$ .	Conc. $NaNO_3$ .	$K_1$ .
0.01	0.1	0.15
0.01	1.0	0.15
0.05	—	0.11
0.25	—	0.33
0.40	—	0.46
1.0	—	4.0

As  $K_1$  increased rapidly with increase in  $c$ , Lewis plotted  $K_1$  against  $c$ , and found that the values of  $K_1$  with the exception of the last one could be expressed empirically as a linear function of  $c$ , namely

$$K_1 = 0.14 \times 0.77c$$

Lewis now substituted the right-hand side of this expression in his equation, and showed that the expression thus obtained for  $[Pb^{..}]$  in terms of  $e$  and  $K_2$  gave values of  $[Pb^{..}]$  which agreed excellently with those obtained by direct potential measurements. This is shown by the following table:—

$c$ .	$NaNO_3$ .	$e$ .	I.	II.	$\Delta MV$ .
1.0	—	-0.439	0.089	0.083	1
0.4	—	-0.443	0.065	0.065	0
0.25	—	-0.445	0.056	0.056	0
0.05	—	-0.455	0.0255	0.0258	0
0.01	1.0	-0.511	0.000324	0.00033	0
0.01	0.1	-0.479	0.0039	0.0042	1
0.01	—	-0.469	0.0083 <sup>1</sup>	0.0083 <sup>1</sup>	—

$e$  is the potential of the lead electrode with respect to the 1.0 N. calomel electrode at 25°. In Column I. are given the values of  $[Pb^{..}]$  calculated from the potential by means of the formula

$$e = -0.408 + 0.0295 \log [Pb^{..}]$$

In Column II. are the values calculated by means of the substituted equation connecting  $[Pb^{..}]$  and  $e$ , or, in the cases where  $NaNO_3$  is present, from equation (7). The difference in the last column is reckoned in millivolts.

Having thus obtained a satisfactory means of calculating  $[Pb^{..}]$ ,  $[PbNO_3^.]$ , and  $[Pb(NO_3)_2]$  in any solution from a knowledge of the potential of a lead electrode dipping into it, Lewis proceeded to the study of the complex solutions obtained by mixing lead nitrate with potassium nitrate.

The total lead concentration,  $c$ , may be split into the "normal" concentration,  $c_n$ , and the complex lead concentration,  $C$ , so that

$$c = c_n + C$$

where  $c_n = [Pb^{..}] + [PbNO_3^.] + [Pb(NO_3)_2]$

$c_n$  was found from the potential by the method sketched above, and  $C$  was then given by

$$C = c - c_n$$

<sup>1</sup> Starting point of the calculation. These values were taken as equal.

Thus we now have numerical values for  $[Pb^{..}]$ ,  $[NO_3']$ , and  $C$ , and the constitution of the complex can be decided by the method of Bodländer, with the one reservation that it would be difficult to make two solutions in which  $[NO_3']_1$  was not equal to  $[NO_3']_2$ , while  $C_1$  was equal to  $C_2$ . The law of mass action was therefore applied in this way: that the dissociation constant

$$K_3 = \frac{[K^.]^p[Pb^{..}]^q[NO_3']^r}{[K_pPb_q(NO_3)_r]} \quad . \quad . \quad . \quad (8)$$

was calculated for various values of  $p$ ,  $q$ , and  $r$ , and the values of these indices were thus found which gave the best constancy of  $K_3$ . All the measurements were made with solutions in which the potassium nitrate was in large excess compared with the lead nitrate, so that  $[K^.]$  could be set equal to  $[NO_3']$ . The results appear to show that  $p$ ,  $q$ , and  $r$  are each equal to 1, though unfortunately the constancy of  $K_3$  was in no case very satisfactory. The mean value was taken as 0.036.

Using the numerical values of  $K_1$ ,  $K_2$ , and  $K_3$ , we can calculate theoretically the concentration of lead ions in any mixture of lead and potassium nitrates, and by comparing these with the values found by measurements of the potential of the lead electrode we can thus check the accuracy of our conclusions. The calculation is carried out as follows:—

For the mixed solution the following equations hold:—

$$K_1 = \frac{[PbNO_3^.] [NO_3']}{[Pb(NO_3)_2]} = 0.14 + 0.77c \quad . \quad (1)$$

$$K_2 = \frac{[Pb^{..}] [NO_3']}{[PbNO_3^.] } = 0.11 \quad . \quad . \quad . \quad (2)$$

$$K_3 = \frac{[Pb^{..}] [NO_3'] [K^.] }{[PbNO_3K^{..}]} = 0.036 \quad . \quad . \quad . \quad (8)$$

$$[PbNO_3K^{..}] + [Pb^{..}] + [PbNO_3^.] + [Pb(NO_3)_2] = c \quad . \quad (9)$$

Combining these we obtain

$$[Pb^{..}] = \frac{c}{\frac{[K^.] [NO_3']}{K_3} + \frac{[NO_3']^2}{K_1 K_2} + \frac{[NO_3']}{K_2} + 1} \quad (10)$$

The values of  $[Pb^{..}]$  in a number of mixed solutions in which the concentrations of the two salts varied between wide limits were calculated by means of equation (10), and showed very close agreement with the values obtained by potential measurements, the difference between the two values in no case amounting to more than two millivolts.

It was also shown that the general behaviour of the solubilities was such as to support the foregoing conclusions, namely, that in mixed solutions of lead and potassium nitrates the complex ion  $[PbNO_3K^{..}]$  is formed.

A somewhat similar method of attack was used by Jaques (*loc. cit.*) in investigating the complex formation occurring in solutions of lead and cadmium acetates. In each case  $K_2$  was determined from potential measurements by means of Lewis's equation, and it was found by means of freezing-point experiments that  $K_1$  was sufficiently large to ensure that  $\frac{2[Pb^{..}]^2}{K_1}$  could be neglected in comparison with  $c$ ,

$K_1$  was found more accurately by the solubility method, using the value of  $K_2$  already found. Since both lead and cadmium acetate are too soluble to allow of the application of the law of mass action to their own solubilities, the method was reversed, and the solubility of silver acetate, which is small, was determined in solutions of the two salts to be experimented upon. Measurements of the solubility of silver acetate in solutions of sodium and potassium acetates showed that silver acetate does not form complex ions with additional acetate ions that may be present to any measurable extent.

The calculation of  $K_1$  is carried out as follows:—

We have first

$$\frac{[PbAc^{.}][Ac']}{[PbAc_2]} = K_1 \quad . \quad . \quad . \quad . \quad (1)$$

$$\frac{[Pb^{..}][Ac']}{[PbAc^{.}]} = K_2 \quad . \quad . \quad . \quad . \quad (2)$$

Next, calling the solubility of silver acetate in a lead acetate solution  $\eta$ , we have

$$\eta + 2c = [\text{AgAc}] + [\text{PbAc}\cdot] + 2[\text{PbAc}_2] + [\text{Ac}'] \quad (3)$$

Also, since the solution is electrostatically neutral

$$[\text{Ag}\cdot] + [\text{PbAc}\cdot] + 2[\text{Pb}\cdot\cdot] = [\text{Ac}'] \quad (4)$$

From (2) and (4)

$$[\text{Ac}'] - [\text{Ag}\cdot] = [\text{PbAc}\cdot] \left( 1 + \frac{2K_2}{[\text{Ac}']} \right)$$

whence 
$$[\text{PbAc}\cdot] = \frac{[\text{Ac}'] - [\text{Ag}\cdot]}{1 + \frac{2K_2}{[\text{Ac}']}} \quad (5)$$

From (3)

$$[\text{PbAc}_2] = \frac{\eta + 2c - [\text{AgAc}] - [\text{PbAc}\cdot] - [\text{Ac}']}{2}$$

We thus find  $[\text{Pb}\cdot\cdot]$ ,  $[\text{PbAc}\cdot]$ , and  $[\text{PbAc}_2]$  in terms of  $[\text{Ac}']$ ,  $[\text{AgAc}]$ , and  $[\text{Ag}\cdot]$ . These latter values are found by determining the molecular electrical conductivity  $\Lambda$ , of the silver acetate in saturated solution in water, and using the values given by Loeb and Nernst (*Zeit. phys. Chem.*, **2**, 948 (1888)) for its conductivity at infinite dilution,  $\Lambda_\infty$ .  $\gamma$ , the degree of dissociation, is given by

$$\gamma = \frac{\Delta}{\Delta_\infty}$$

and  $[\text{Ag}\cdot]$  by

$$[\text{Ag}\cdot] = \gamma s$$

where  $s$  is the solubility of the salt in water. The solubility product,  $L$ , is found from the equation

$$L = (\gamma s)^2$$

and the value of the concentration  $[\text{AgAc}]$  is obtained from the equation

$$[\text{AgAc}] = s - [\text{Ag}\cdot]$$

$L$  and  $[\text{AgAc}]$  are constant in all saturated solutions, and we may, therefore, use the values we have found in investigating the solutions containing lead or cadmium acetate.

Dealing now with the mixed solutions, we have

$$[\text{Ag}'] = \eta - [\text{AgAc}]$$

and

$$[\text{Ac}'] = \frac{L}{[\text{Ag}']}$$

We are thus in a position to obtain numerical values for  $[\text{PbAc}']$ ,  $[\text{Ac}']$ , and  $[\text{PbAc}_2]$  in the mixed solutions, and can, therefore, calculate the value of  $K_1$  from equation (1). The accompanying table shows the results obtained, using the values  $[\text{AgAc}] = 0.0172$  and  $L = 0.00242$ .

c (lead acetate).	$\eta$ .	$\eta - [\text{AgAc}] = [\text{Ag}']$ .	$\frac{L}{[\text{Ag}']} = [\text{Ac}']$ .	$[\text{PbAc}']$ .	$[\text{PbAc}_2]$ .	$K_1$ .
1.0	0.03587	0.01867	0.1297	0.1077	0.8906	0.0157
0.5	0.04349	0.02631	0.0921	0.0630	0.4356	0.0133
0.1	0.04995	0.03275	0.0739	0.0391	0.0599	0.0482
0.05	0.0566	0.0394	0.0614	0.0207	0.0286	0.0444
0.01	0.06403	0.0468	0.0517	0.00452	0.00530	0.0441

The last three values of  $K_1$ , *i.e.* those obtained in dilute solutions, show a fair degree of constancy. All work of this kind suffers from the large number of experimental values that have to be introduced into the calculations.

The mean value of  $K_1$  was now substituted in Lewis's equation, which was solved without approximation for  $K_2$ , with the result that  $K_2$  was found to have the value 0.0021 instead of 0.0020, the provisional value used in calculating  $K_1$ .

As in Lewis's work, the calculations were now applied to the complex solutions, and the concentration,  $C$ , of the lead present as complex was determined.

The values of  $q$  and  $r$  in the equation

$$\frac{[\text{Pb}']^q [\text{Ac}']^r}{[\text{Pb}_q \text{Ac}_r]} = K_3$$

were now calculated. These had already been worked out by means of Bodländer's theorem, on the assumption that all the lead was in the form of the complex ion.  $q$  was found to be 1, while  $r$  varied rapidly with the concentration

of the alkaline acetate. It was now found that in solutions of equal acetate ion concentration  $C$  was proportional to  $c$ , so that

$$\frac{[\text{PbAc}_r]_1}{[\text{PbAc}_r]_2} = \frac{C_1}{C_2} = \frac{c_1}{c_2}$$

Thus the value of  $q$  is unaffected by taking into consideration the incompleteness of the complex formation, but the value of  $r$ , on the other hand, is considerably affected.

Instead of calculating the constant  $K_3$  for various values of  $r$  ( $q$  being known to be 1), the method of Bodländer was extended in the manner described in Chapter VI to the case where  $[\text{PbAc}_r]_1$ ,  $[\text{PbAc}_r]_2$ ,  $[\text{Ac}]_1$ , and  $[\text{Ac}]_2$  are all unequal.

In the case of lead acetate the values of  $r$  increased rapidly with increasing acetate ion concentration, but even in the more dilute solutions (0.279 and 0.673 N. solutions of sodium acetate) the values lay between 3 and 4. If we plot  $r$  against the mean value of  $[\text{Ac}]_1$  and  $[\text{Ac}]_2$  we find that when  $[\text{Ac}]_1$  and  $[\text{Ac}]_2$  become indefinitely small,  $r$  becomes approximately 3. Thus the ion  $\text{PbAc}'_3$  is probably formed, and possibly an ion or ions containing more acetate ions such as  $\text{PbAc}_4''$ , but the high values of  $r$  in the strong solutions of alkali acetate must be regarded as probably due to disturbing influences such as, possibly, hydrate formation. (See Appendix I.)

The behaviour of cadmium acetate solutions was precisely similar.

For an examination of mixed solutions of zinc and mercuric chlorides, and of the dissociation of zinc chloride, barium chloride and barium bromide, the reader is referred to Drucker, *Zeit. Elektrochemie*, **18**, 236 (1912), and **19**, 797 (1913).

## CHAPTER VIII

### AMMONIACAL SALT SOLUTIONS, ETC.

FROM the well-known fact that silver chloride, a substance which is very slightly soluble in water, dissolves freely in ammonia solution, we may at once conclude that chemical combination occurs, and the reaction consists, presumably, in the formation of a complex ion. Since all silver salts show the property of being relatively much more soluble in ammonia than in water, whilst this is not the case with all chlorides, it appears that the complex ion is formed by the combination of the silver ion with ammonia. This is further supported by the fact that the silver ions as such disappear during the reaction, while the anion (single ion) does not.

During the last fifteen years the constitution of silver-ammonia solutions has been the subject of much study which has yielded interesting and remarkable results.

Bodländer (*Zeit. phys. Chem.*, **9**, 730 (1892)) obtained and analysed unstable crystals from a solution of silver chloride in ammonia. Their composition corresponded to the formula  $2\text{AgCl}, 3\text{NH}_3$ . He further determined the solubility of silver chloride in solutions of ammonia of various strengths, and found that the solubility rose rapidly as the concentration of ammonia was increased until the latter reached a value of about 5 N., when the solubility of silver chloride became nearly constant. This concentration of ammonia (5 N.) is also that at which it becomes possible to obtain the crystalline compound.

Later (*Zeit. phys. Chem.*, **39**, 597 (1902)) Bodländer and Fittig studied the matter further, with very curious results.



These will be referred to after we have considered the work of some other observers.

Reychler (*Bull. de la Soc. Chim. de Paris*, **13**, 386 (1895)) found that addition of ammonia to solutions of silver nitrate, silver acetate, silver sulphate, and silver nitrite had no effect upon the freezing point until two molecules of ammonia had been added for each atom of silver present. Further addition of ammonia caused a normal depression.

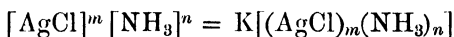
Konowalaw (*Chem. Zentralblatt*, 1898, II, 659) measured the pressure of ammonia over solutions to which successive quantities of silver nitrate were added, and found that the pressure was diminished to the extent that would correspond to the removal of two molecules of ammonia from the solution for each molecule of silver nitrate added.

Dawson and McCrae (*Zeit. anorg. Chem.*, **26**, 94 (1901)) measured the distribution coefficient of ammonia between chloroform and water, and found that on adding silver chloride to the water about  $1\frac{1}{2}$  molecules of ammonia disappeared for each molecule of silver chloride added.

Gaus (*Zeit. anorg. Chem.*, **25**, 236 (1900)) in the course of an investigation of the effect of a number of salts on the pressure of ammonia over ammonia solutions, found that in a 1.0 N. ammonia solution saturated with silver chloride (0.0491 N. with respect to AgCl) the pressure was reduced to an extent corresponding to the removal of two molecules of ammonia for each atom of silver present, calculating according to Henry's law, *i.e.* that the ammonia pressure was proportional to the concentration; and he had already shown by preliminary experiments that ammonia solutions obey Henry's law very closely.

Bodländer and Fittig (*loc. cit.*) now made an exhaustive study of the subject, which we shall describe shortly.

We may express the formation of the complex by means of the scheme



which is the equation determining the equilibrium between

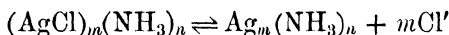
*undissociated* silver chloride and an *undissociated* complex salt. Thus, if we work in solutions saturated with respect to silver chloride,

$$[\text{AgCl}]^m \Rightarrow \text{const.}$$

and we obtain

$$[\text{NH}_3]^n = K_1[(\text{AgCl})_m(\text{NH}_3)_n] = K_1 D$$

where  $K_1$  is a constant and  $D$  is the concentration of the *undissociated complex salt*. From previous knowledge of the behaviour of complex silver solutions we may assume that the complex salt dissociates into a complex kation containing  $m$  atoms of silver, and  $m$  chlorine ions according to the scheme



the kation having  $m$  positive charges. Thus

$$D = [(\text{AgCl})_m(\text{NH}_3)_n] = k[\text{Ag}_m(\text{NH}_3)_n][\text{Cl}']^m$$

If the degree of dissociation of the complex salt be  $\alpha$ , and its total concentration  $D_1$ ,

$$D = (1 - \alpha)D_1$$

and 
$$D = k(\alpha D_1)(\alpha D_1)^m = k(\alpha D_1)^{m+1}$$

Also 
$$[\text{NH}_3]^n = K_1 D = K_1 k(\alpha D_1)^{m+1} = k_1(\alpha D_1)^{m+1}$$

Hence 
$$[\text{NH}_3] = \sqrt[n]{k_1} \cdot (\alpha D_1)^{\frac{m+1}{n}}$$

[NOTE.—The original paper contains a very confusing slip, the symbol  $D$  being used throughout for both the concentration of the undissociated complex salt and for the total complex concentration without remark. Thus the calculation in the paper appears to contain an error. The above expression is applied to the experimental results, however, using the total complex concentration in place of the quantity we have called  $D_1$ , which, as we have seen, is correct.]

The method followed consisted in determining the solubility of silver chloride in various solutions of ammonia, choosing ratios of the values of  $n$  and  $m + 1$ , and discovering the correct ratio by trial. Only the ratio  $\frac{m+1}{n}$  can be

found in this way, for clearly a series of values of  $m$  and  $n$  will fit the equation

$$[\text{NH}_3] = \sqrt[n]{k_1 \cdot (aD_1)^{\frac{m+1}{n}}}$$

for any value of the ratio. Thus  $m$  and  $n$  cannot be determined separately by this method.

As the balance of evidence by previous observers (Reychler, Konowalaw and Gaus as against Dawson and McCrae) favoured the formula  $\text{AgCl}_2\text{NH}_3$ , the values  $n = 2$ ,  $m = 1$  were tried first, and  $a$  was taken as the degree of dissociation of a binary salt, values of  $a$  being chosen corresponding to those for the alkali chlorides. The concentration of free ammonia was calculated on the assumption that two molecules of ammonia combined with one molecule of silver chloride, in accordance with the above values of  $m$  and  $n$ .

For this ratio of  $m$  and  $n$  we have

$$\sqrt[k_1]{[\text{NH}_3]} = \frac{[\text{NH}_3]}{D_1 a}$$

The solubility of silver chloride in ammonia solutions was determined at 25° with the following results:—

TABLE A.

1000 grams of water contain mols.		Conc. free $\text{NH}_3$ .	Active mass of $\text{NH}_3$ = $\Lambda$ .	$\alpha$ .	$\alpha'$ .	$\sqrt[k_1]{}$	
$\text{NH}_3$ .	$\text{AgCl} = D_1$ .					$= \frac{\Lambda}{D_1 \alpha}$ .	$= \frac{\Lambda}{D_1 \alpha'}$ .
0.0942	0.004592	0.0850	0.0852	0.95	0.95	19.55	19.55
0.10065	0.005164	0.0903	0.0906	0.95	0.95	18.47	18.47
0.1033	0.005343	0.0926	0.0929	0.95	0.95	18.31	18.31
0.2084	0.01137	0.1857	0.1868	0.94	0.91	17.56	18.05
0.2947	0.01588	0.2629	0.2653	0.93	0.88	18.04	18.98
0.4881	0.02588	0.4364	0.4427	0.91	0.85	18.80	20.12
0.7522	0.04758	0.6570	0.6714	0.89	0.80	15.85	17.64
0.9663	0.06117	0.8440	0.8675	0.87	—	16.23	—
1.9004	0.13616	1.6281	1.7150	0.84	—	14.95	—
2.8393	0.2254	2.3885	2.5767	0.82	—	14.02	—
3.7574	0.3438	3.0698	3.3808	0.80	—	12.36	—
4.6918	0.4680	3.7558	4.2212	0.78	—	11.57	—

The active mass of ammonia (A) was taken as being proportional to its gaseous pressure. The relation between the gaseous pressure ( $p$ ) and the number of gram molecules of ammonia per 1000 grams of water ( $n$ ) was determined by Gaus (*loc. cit.*), who found that it could be expressed by the equation

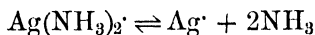
$$\frac{p}{n} = 12.59(1 + 0.033n)$$

Thus the active mass, A, is given by

$$A = n(1 + 0.033n)$$

Although the constant shows a small progressive change in the very strong solutions, it is clear from the results that  $\frac{m+1}{n} = 1$ . Other ratios were tried, but the constant changed very rapidly. The calculations were carried out with values of  $a$  for a binary salt, but actually the value 1 for the ratio would also correspond to the salt  $2\text{AgCl}, 3\text{NH}_3$ , and generally to salts of the type  $(\text{AgCl})_m(\text{NH}_3)_{m+1}$ . If such salts were formed, however, they would probably dissociate to a smaller extent. For example, the salt  $2\text{AgCl}, 3\text{NH}_3$  would probably dissociate to the same extent as other ternary electrolytes, such as zinc chloride. It is therefore probable on these grounds that the salt formed has the formula  $\text{AgCl}, 2\text{NH}_3$ ; and as subsequent experiments showed that the formula  $2\text{AgCl}, 3\text{NH}_3$  was not possible, the calculations were not carried further.

Another method was now applied, by means of which it was shown that the complex salt has not the constitution expressed by the formula  $2\text{AgCl}, 3\text{NH}_3$ . If the salt has the formula  $\text{AgCl}, 2\text{NH}_3$ , it will form the kation  $\text{Ag}(\text{NH}_3)_2^+$ , and this in turn will dissociate according to the scheme



This dissociation occurs to a very minute extent, so that we may write

$$[\text{Ag}(\text{NH}_3)_2^+] = aD_1$$

Hence

$$k_2 D_1 a = [\text{Ag}^+][\text{NH}_3]^2$$

Now, in solutions saturated with silver chloride, the solubility product  $[Ag^+][Cl^-]$  is constant, therefore

$$K_2 a D_1 = \frac{[NH_3]^2}{[Cl^-]}$$

Similarly, if the complex salt had the formula  $2AgCl, 3NH_3$ , we should have

$$K_3 a D_1 = \frac{[NH_3]^3}{[Cl^-]^2}$$

Thus by measuring the solubility of silver chloride in solutions of ammonia containing various amounts of chlorine ions we can distinguish between the two formulæ. Table B shows the results of such a series of determinations.

TABLE B.

1000 grams of water contain mols.			Active mass of ammonia		a.	$\sqrt{K_2}$ .	$\sqrt{K_3}$ .
$NH_3$ .	$AgCl$ .	$KCl$ .	A.	$A_1$ .			
0.7522	0.04875	0.0	0.6716	0.6978	0.89	15.87	66.7
0.7477	0.04392	0.0102	0.6740	0.6981	0.88	15.73	63.3
0.7458	0.03869	0.0255	0.6833	0.7036	0.87	15.78	58.4
0.7497	0.03330	0.0511	0.6990	0.7175	0.86	15.71	49.4

As before, A is the active mass of ammonia, calculated on the assumption that two molecules of ammonia combine with one molecule of silver chloride.  $A_1$  is the active mass of ammonia, calculated on the assumption that three molecules of ammonia combine with two molecules of silver chloride, in accordance with the second scheme.  $a$  is Kohlrausch's value for the degree of dissociation if all the chlorine present were in the form  $KCl$ . Thus  $[Cl^-]$  is given in the first case by

$$[Cl^-] = a(D_1 + C_{KCl})$$

where  $C_{KCl}$  = concentration of  $KCl$  added, and in the second case by

$$[Cl^-] = 2a \cdot \frac{D_1}{2} + aC_{KCl}$$

*i.e.* it has the same value in the two cases. In the second case  $\alpha$  would probably have the value for a ternary electrolyte instead of that for a binary one, but addition of small quantities of potassium chloride would not alter its value in a manner very different from that for a binary electrolyte. These results, therefore, show beyond doubt that the complex salt is not that represented by the formula  $2\text{AgCl}, 3\text{NH}_3$ , and that it is to be represented by the formula  $m\text{AgCl}, n\text{NH}_3$ , where  $n = 2m$ . Since we have proved that  $n = m + 1$ , it follows that  $m$  must be equal to 1 and  $n$  must be equal to 2. An inspection of the calculations in the two cases—with and without addition of potassium chloride—shows that  $K_2$  in Table B is the same constant as  $k_1$  in Table A. The experiments show that it has the same value in the two cases.

Similar measurements were next made with addition of silver nitrate instead of potassium chloride. If the complex formation is confined exclusively to the silver and ammonia, the same complex kation should be formed when any other silver salt is present. If the kation be  $\text{Ag}(\text{NH}_3)_2^+$ , we have, as before,

$$k_2[\text{Ag}(\text{NH}_3)_2^+] = [\text{Ag}^+][\text{NH}_3]^2$$

In presence of solid silver chloride,

$$[\text{Ag}^+][\text{Cl}'] = \text{const.}$$

and thus 
$$K_2[\text{Ag}(\text{NH}_3)_2^+] = \frac{[\text{NH}_3]^2}{[\text{Cl}']}$$

Since the chlorine ions are practically all produced by the dissociation of the complex salt—the solubility of silver chloride in water being negligibly small compared with its solubility in these solutions—we may put

$$[\text{Cl}'] = D_1\alpha$$

$D_1$ , as before, being equal to the total concentration of silver chloride dissolved. Also, calling the total silver concentration  $c$ , we have

$$[\text{Ag}(\text{NH}_3)_2^+] = \alpha c$$

$\alpha$  being taken without considerable error as the degree of

dissociation of a salt of concentration  $c$ : that is, the complex chloride and the complex nitrate being treated as a single salt. Thus we get

$$K_2 = \frac{A^2}{a^2 c D_1}$$

or

$$\sqrt{K_2} = \frac{A}{a \sqrt{c D_1}}$$

from which it is obvious that addition of silver nitrate should cause a depression in the solubility of silver chloride in ammonia in a somewhat similar manner to potassium chloride.

Accordingly, the solubility of silver chloride was determined in various solutions of ammonia and silver nitrate, ammonia being in excess. In calculating the concentration of free ammonia we must remember that silver chloride and silver nitrate each combines with two molecules of ammonia. The results are shown in Table C, and show excellent agreement with the theory.

TABLE C.

1000 grams of water contain mols.			A	a.	$\sqrt{K_2}$ .
NH <sub>3</sub> .	AgCl.	AgNO <sub>3</sub> .			
0.7522	0.04758	0.0	0.6715	0.89	15.87
0.7517	0.04173	0.01021	0.6617	0.88	16.14
0.7503	0.03503	0.02556	0.6423	0.87	16.02
0.7550	0.02751	0.05129	0.6093	0.87	15.45

As a further check upon the conclusions drawn we may proceed to calculate the solubility of any other silver salt, such as the bromide, in ammonia solutions if its solubility in water is known; or conversely, if we know its solubility in ammonia solutions we may calculate its solubility in water in terms of the solubility of silver chloride.

Considering the case of silver chloride and silver bromide, for each salt

$$k_2 = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

For the two salts we have further, respectively,

$$[\text{Ag}^+] = \frac{L_{\text{AgCl}}}{[\text{Cl}']}$$

and

$$[\text{Ag}^+] = \frac{L_{\text{AgBr}}}{[\text{Br}']}$$

where  $L_{\text{AgCl}}$  and  $L_{\text{AgBr}}$  are the solubility products.

Further,

$$[\text{Cl}'] = [\text{Ag}(\text{NH}_3)_2^+]_{\text{AgCl}}$$

and

$$[\text{Br}'] = [\text{Ag}(\text{NH}_3)_2^+]_{\text{AgBr}}$$

in the two solutions in ammonia, when no other salt is present.

Thus

$$k_2 = \frac{L_{\text{AgCl}}[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]^2_{\text{AgCl}}} = \frac{L_{\text{AgBr}}[\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]^2_{\text{AgBr}}}$$

Now

$$[\text{Ag}(\text{NH}_3)_2^+] = aD_1$$

so that

$$k_2 = \frac{L_{\text{AgCl}}[\text{NH}_3]^2}{(aD_1)^2_{\text{AgCl}}} = \frac{L_{\text{AgBr}}[\text{NH}_3]^2}{(aD_1)^2_{\text{AgBr}}}$$

or

$$\sqrt{k_2} = \frac{\sqrt{L_{\text{AgCl}}[\text{NH}_3]}}{(aD_1)_{\text{AgCl}}} = \frac{\sqrt{L_{\text{AgBr}}[\text{NH}_3]}}{(aD_1)_{\text{AgBr}}}$$

Now,

$$\frac{[\text{NH}_3]}{(aD_1)_{\text{AgCl}}} = \frac{A}{(aD_1)_{\text{AgCl}}} = \sqrt{k_1} \quad (\text{Table A}).$$

and

$$\frac{[\text{NH}_3]}{(aD_1)_{\text{AgBr}}} = \frac{A}{(aD_1)_{\text{AgBr}}} = \sqrt{k_1} \quad (\text{Table D}).$$

Hence

$$\sqrt{L_{\text{AgCl}}}\sqrt{k_{1\text{AgCl}}} = \sqrt{L_{\text{AgBr}}}\sqrt{k_{1\text{AgBr}}}$$

i.e.

$$\frac{\sqrt{L_{\text{AgCl}}}}{\sqrt{L_{\text{AgBr}}}} = \frac{\sqrt{k_{1\text{AgBr}}}}{\sqrt{k_{1\text{AgCl}}}} \quad (\text{A}).$$

or

$$\sqrt{L_{\text{AgBr}}} = \sqrt{L_{\text{AgCl}}} \cdot \frac{\sqrt{k_{1\text{AgCl}}}}{\sqrt{k_{1\text{AgBr}}}} \quad (\text{B}).$$



Table D shows the values of  $\sqrt{k_{1\text{AgBr}}}$  obtained as in the case of silver chloride. The mean value is 322.5.

TABLE D.

1000 grams water contained mols.		$\Lambda$ .	$\alpha$ .	$\sqrt{k_1} = \frac{\Lambda}{D_1\alpha}$
$\text{NH}_3$ .	$\text{AgBr}$ .			
0.1932	0.00060	0.1933	0.99	325.4
0.3849	0.00120	0.3874	0.98	329.3
0.5741	0.00179	0.5813	0.97	334.9
0.7573	0.00223	0.7716	0.96	360.4
1.965	0.00692	2.0780	0.94	319.6
3.024	0.01163	3.301	0.93	307.7
5.244	0.02443	6.093	0.91	280.4

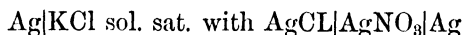
Mean = 322.5

Bodländer and Fittig took as the weighted mean of the values of  $k_{1\text{AgCl}}$  in Table A the value 18.46. This gives

$$\sqrt{L_{\text{AgBr}}} = \sqrt{L_{\text{AgCl}}} \cdot \frac{18.46}{322.5}$$

Now,  $\sqrt{L_{\text{AgBr}}}$  and  $\sqrt{L_{\text{AgCl}}}$  are the solubilities of silver chloride and bromide respectively in water, since the dissociation of these salts is practically complete.

Goodwin (*Zeit. phys. Chem.*, **13**, 645 (1894)) measured the potential of cells of the type



and was thus able to calculate the solubility product  $[\text{Ag}^+][\text{Cl}^-]$ . He found  $\sqrt{L_{\text{AgCl}}} = 1.25 \times 10^{-5}$  gram molecule per litre at 25°. Using this value, we find

$$\sqrt{L_{\text{AgBr}}} = 7.15 \times 10^{-7} \text{ gram mols. per litre (Equation B)}$$

From potential measurements Goodwin found

$$\sqrt{L_{\text{AgBr}}} = 6.6 \times 10^{-7} \text{ gram mols. per litre}$$

Kohlrausch and Dolezalek (*Sitzungsber. der Berl. Akad. d. Wiss.*, 1901, 101) found the solubility of silver bromide at 25° to be  $7.1 \times 10^{-7}$  gram mols. per litre.

Thiel (*Diss. Giessen*, 1900) found the solubilities at  $25^\circ$  to be  $1.41 \times 10^{-5}$  and  $8.1 \times 10^{-7}$  gram mols. per litre, respectively, giving the ratio  $\sqrt{L_{\text{AgCl}}}/\sqrt{L_{\text{AgBr}}} = 17.4 : 1$ . The ratio calculated from the values of  $k_{1\text{AgCl}}$  and  $k_{1\text{AgBr}}$  is  $17.5 : 1$  (Equation A).

Thus the theoretical treatment of the equilibria which was applied to the case of silver chloride is fully borne out in the case of silver bromide.

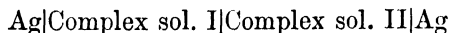
Similarly we can now calculate the solubility in ammonia solutions of any silver salt whose solubility in water is known. For example, Goodwin found that the solubility of silver iodide in water at  $25^\circ$  was  $0.97 \times 10^{-8}$  gram mol. per litre. Now

$$\begin{aligned} k_{1\text{AgI}} &= \frac{\sqrt{L_{\text{AgCl}}}}{\sqrt{L_{\text{AgI}}}} \cdot \sqrt{k_{1\text{AgCl}}} \\ &= \frac{1.25 \times 10^{-5}}{0.97 \times 10^{-8}} \times 18.46 = 24,000 \end{aligned}$$

Hence 
$$\frac{[\text{NH}_3]}{\text{Solubility of AgI in ammonia}} = 24,000$$

or a litre of normal ammonia solution would dissolve  $\frac{1}{24,000}$  gram molecule, or 0.0141 (more exactly) *gram* of silver iodide.

Bodländer and Fittig also examined solutions of silver chloride and silver nitrate in ammonia by the potential method, and the results showed that one silver ion combines with two molecules of ammonia, in agreement with the foregoing results. The cells measured were of the type



The liquid potential was not taken into account.

It is interesting to compare the values of the dissociation constant

$$k_2 = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

obtained by the solubility and potential methods.

In the case of the solubility measurements we have

$$k_1 = \frac{[\text{NH}_3]^2}{(aD_1)^2}$$

and

$$k_2 = \frac{L_{\text{AgCl}}[\text{NH}_3]^2}{(aD_1)^2}$$

Thus

$$k_2 = L_{\text{AgCl}} \cdot k_{1\text{AgCl}}$$

Taking Thiel's values for  $L_{\text{AgCl}}$  and  $L_{\text{AgBr}}$  ( $1.41 \times 10^{-5}$ )<sup>2</sup> and  $(8.1 \times 10^{-7})^2$  respectively, we obtain

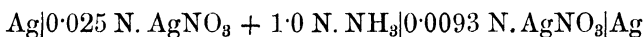
$$k_2 = 6.77 = 10^{-8}$$

and

$$k_2 = 6.82 = 10^{-8}$$

from the results with silver chloride and silver bromide—a truly excellent agreement.

In the case of the potential measurements, the E.M.F. of the cell



was 0.3879 volt. Neglecting the liquid potential, we find for the concentration of free silver ions in the ammoniacal solution, the value  $1.793 \times 10^{-9}$  gram ion per litre. In the equation

$$k_2 = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]}$$

$[\text{NH}_3] = 1.022$  and  $[\text{Ag}(\text{NH}_3)_2^+] = 0.025 \times 0.95$ , taking 0.95 as the degree of dissociation of the complex salt  $\text{Ag}(\text{NH}_3)_2\text{NO}_3$ . Hence

$$k_2 = 7.88 \times 10^{-8}$$

in very satisfactory agreement with the values found from the solubility measurements.

Bodländer and Fittig thus accumulated a very strong mass of evidence for the existence in solution of the complex ion  $\text{Ag}(\text{NH}_3)_2^+$ . On the other hand, the only complex salt which Bodländer was able to obtain in a solid form from the silver chloride solution had the composition  $2\text{AgCl} \cdot 3\text{NH}_3$ . This is also the compound formed when gaseous ammonia reacts with dry silver chloride, within wide limits of pressure. How are we to explain the anomaly?

Many solid silver salts are known which do contain two molecules of ammonia to each silver atom, such as  $\text{AgI}, 2\text{NH}_3$ ;  $\text{AgClO}_3, 2\text{NH}_3$ ;  $\text{AgBrO}_3, 2\text{NH}_3$ ;  $\text{Ag}_2\text{SO}_4, 4\text{NH}_3$ ;  $\text{Ag}_2\text{S}_2\text{O}_7, 4\text{NH}_3$ ;  $\text{Ag}_2\text{SeO}_4, 4\text{NH}_3$ ;  $\text{Ag}_2\text{CrO}_4, 4\text{NH}_3$ ;  $\text{AgNO}_3, 2\text{NH}_3$ ;  $\text{AgNO}_2, 2\text{NH}_3$ ;  $\text{Ag}_4\text{As}_2\text{O}_5, 8\text{NH}_3$ ;  $\text{AgC}_2\text{H}_3\text{O}_2, 2\text{NH}_3$ ;  $\text{Ag}_2\text{C}_2\text{O}_4, 4\text{NH}_3$ ;  $\text{Ag}_3\text{C}_6\text{H}_5\text{O}_7, 6\text{NH}_3$  (citrate);  $\text{AgC}_6\text{H}_5\text{CO}_2, 2\text{NH}_3$ ;  $\text{AgC}_6\text{H}_2(\text{NO}_2)_3\text{O}, 2\text{NH}_3$ . In addition, however, the following salts containing ammonia are known, and no indication has been obtained of their existence in solution:  $2\text{AgCl}, 3\text{NH}_3$ ;  $2\text{AgBr}, 3\text{NH}_3$ ;  $\text{AgBr}, \text{NH}_3$ ;  $\text{AgI}, \text{NH}_3$ ;  $2\text{AgI}, \text{NH}_3$ ;  $\text{AgNO}_3, \text{NH}_3$ ;  $\text{AgNO}_2, \text{NH}_3$ ;  $\text{Ag}_3\text{C}_3\text{N}_3\text{O}_3, \text{NH}_3$ ;  $\text{AgCNS}, \text{NH}_3$ .

Some salts are also known which contain more than two molecules of ammonia to one atom of silver, such as  $\text{AgCl}, 3\text{NH}_3$ ;  $\text{AgBr}, 3\text{NH}_3$ ;  $\text{AgNO}_2, 3\text{NH}_3$ ;  $\text{AgNO}_3, 3\text{NH}_3$  (see Reychler, *Les Dérivés ammoniacaux des sels d'argent*, Bruxelles, 1884; Joannis and Crozier, *Comptes Rendus*, **118**, 1149 (1894)). Thus it would appear that the existence of a solid salt affords little evidence as to the state of affairs in a solution from which it crystallises. This is fully borne out by theoretical considerations. The point was discussed in a very illuminating manner by Abegg and Hamburger (*Zeit. anorg. Chem.*, **50**, 403), who point out that the deposit from a solution must always consist of the substance whose saturation concentration is first reached at the temperature of the experiment. The question as to what substance will crystallise from a complex solution is thus purely one of solubilities and the equilibria existing in the solution. Thus a compound of small solubility may crystallise from a solution in which it is present only to a minute extent in equilibrium with large quantities of other substances. It must be noticed that the solubility we refer to here means the concentration in the solution of the molecules which form the solid, and not the apparent solubility we should find if we shook up the solid with water until no more would dissolve. In the latter case we should obtain a solution, saturated indeed with the molecules of which the solid was composed, but containing besides other products

formed by the partial dissociation of these molecules and the subsequent partial recombination of the products in different proportions. The compound in question,  $2\text{AgCl}$ ,  $3\text{NH}_3$ , can only be obtained from strong ammonia solutions, so that if we shook it up with water silver chloride would separate until the ammonia concentration was great enough to hold the remaining silver chloride in solution in the form  $\text{AgCl}\cdot 2\text{NH}_3$ .

There is thus no real anomaly in the case, and the behaviour might be expected under suitable circumstances.

Abegg and Cox (*Zeit. phys. Chem.*, **46**, 11 (1903)) made use of Bodländer and Fittig's results in order to determine the solubility of silver thiocyanate. In this case we have

$$k_2 = \frac{[\text{Ag}^+][\text{NH}_3]^2}{[\text{Ag}(\text{NH}_3)_2^+]} = 6.8 \times 10^{-8}$$

Since silver thiocyanate is a very slightly soluble salt we may put

$$[\text{Ag}(\text{NH}_3)_2^+] = [\text{NCS}^-] = c$$

where  $c$  is the solubility of silver thiocyanate in a solution of ammonia. Thus, in such a solution

$$[\text{Ag}^+][\text{NH}_3]^2 = k_2 c$$

and

$$[\text{Ag}^+][\text{NCS}^-] = L$$

Hence

$$\sqrt{L} = \frac{c}{[\text{NH}_3]} \cdot \sqrt{k_2}$$

In this way the solubility of silver thiocyanate in water was determined by measuring its solubility in ammonia solutions. The original paper contains many numerical errors, so the results in the following table have all been recalculated, taking the experimental results as being correctly printed, saving in one case to which attention is drawn. The mean value of  $\frac{10^3 c}{[\text{NH}_3]}$  is almost identical with that used by the authors in calculating the solubility of silver thiocyanate.

Ammonia.	c.	100 α.	Free NH <sub>3</sub> .	Active mass <sup>1</sup> of NH <sub>3</sub> .	$\frac{10^3 c}{[\text{NH}_3]}$ <sup>2</sup>
0.2761	0.001518	95	0.2731 <sup>2</sup>	0.2756 <sup>2</sup>	5.23 <sup>2</sup>
0.4435	0.002139	95	0.4392	0.4455 <sup>2</sup>	4.56 <sup>2</sup>
0.5865	0.00295	95	0.5806	0.5917 <sup>2</sup>	4.73 <sup>2</sup>
1.3247	0.00720	94 <sup>3</sup>	1.3103 <sup>2</sup>	1.367 <sup>2</sup>	4.95 <sup>2</sup>

Mean = 4.87

Thus  $\frac{c}{[\text{NH}_3]} = 4.87 \times 10^{-3}$ . The mean of the values given in the original paper was  $4.5 \times 10^{-3}$ .

Taking  $\frac{c}{[\text{NH}_3]} = 4.87 \times 10^{-3}$ , we find

$$\sqrt{L} = 4.87 \times 10^{-3} \sqrt{6.8 \times 10^{-8}} = 1.27 \times 10^{-6}$$

The value found in the original paper was  $1.25 \times 10^{-6}$ , so that the errors have probably not been due to mistakes in calculation. An examination on similar lines of solutions of silver iodide and potassium iodide, silver thiocyanate and potassium thiocyanate, and of silver cyanide and potassium cyanide, was made by Bodländer and Eberlein (*Zeit. anorg. Chem.*, **39**, 197 (1904)), and of silver cyanide in ammonia by Lucas (*Zeit. anorg. Chem.*, **41**, 193 (1904)).

The last-mentioned paper contains an interesting point which we may briefly refer to. Lucas found that his experimental values for the solubility of silver cyanide in ammonia could only be explained by supposing that the complex salt which yielded the ions  $\text{Ag}(\text{NH}_3)_2^+$  and  $\text{Ag}(\text{CN})_2^-$  was only slightly dissociated. The degrees of dissociation were calculated for a number of solutions of ammonia saturated with silver cyanide, which would bring his values into

<sup>1</sup> Calculated by means of Gaus' formula (*loc. cit.*).

<sup>2</sup> Differs from the value in original paper.

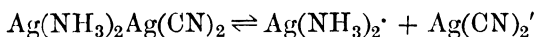
<sup>3</sup> Given as 97 in original paper.

accord with the results of Bodländer and Fittig, and the dissociation constants

$$K_1 = \frac{[\text{Ag}(\text{NH}_3)_2'] [\text{Ag}(\text{CN})_2']}{[\text{Ag}(\text{NH}_3)_2 \text{Ag}(\text{CN})_2]}$$

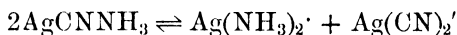
$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2'] [\text{Ag}(\text{CN})_2']}{[\text{AgCnNH}_3]^2}$$

were calculated, corresponding to the schemes



and  $2\text{AgCnNH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2' + \text{Ag}(\text{CN})_2'$   
respectively.

It was found that  $K_2$  showed satisfactory constancy, while  $K_1$  was not at all constant, indicating that the undissociated complex salt has the formula  $\text{AgCnNH}_3$ , and dissociates according to the second of the above schemes. Further support was given to this conclusion by the fact that the degree of dissociation calculated by means of Bodländer and Fittig's results was almost independent of the concentration. This is only possible in the case of salts which dissociate in such a way that the dissociation does not affect the osmotic pressure of the solution—a very unusual condition, which is, however, fulfilled by the reaction



This conclusion completely accounts for the large mass of experimental results obtained by Lucas, and harmonises them perfectly with the observations of Bodländer and Fittig.

An interesting general study of the effects of a large number of salts upon the ammonia pressures of ammonia solutions was made by Gaus (*Zeit. anorg. Chem.*, **25**, 236 (1900)). The method adopted was as follows:—

Electrolytic gas, generated from a cell consisting of nickel electrodes immersed in caustic soda solution, was passed through two large wash-bottles containing the ammonia-salt solution, and then through a conductivity vessel containing a small quantity of dilute (0.01–0.025 N.)

hydrochloric acid. The whole apparatus was placed in a thermostat.

The volume of electrolytic gas used was calculated from the weight of copper deposited in a voltameter which was switched into the circuit at the instant that the gas stream was diverted into the conductivity vessel. Thus by observing the diminution in the conductivity of the hydrochloric acid and the weight of copper deposited in the voltameter, the pressure of ammonia in the gas issuing from the wash-bottles could be calculated. For details of the apparatus and control experiments the reader is referred to the original paper. The first experiments to determine the effect of added salts upon the ammonia pressure were made with salts having an ion in common with the compound  $\text{NH}_4\text{OH}$ , namely, caustic soda on the one hand, and various ammonium salts on the other.

A normal solution of ammonia which was also 0.4 N. with respect to caustic soda had an ammonia pressure of 14.96 mm. at  $25^\circ$ , while the pressure of 1.0 N. ammonia solution alone is 13.45 mm. Thus the caustic soda caused an increase in the ammonia pressure of 1.51 mm., or more than 10 per cent. Gaus considers this increase much too great to be accounted for by diminution in the dissociation of the compound  $\text{NH}_4\text{OH}$ , and suggests that most of it is due to the presence of a second solute, *i.e.* the caustic soda (see Rothmund, *Zeit. phys. Chem.*, **33**, 410 (1900)). It may be added that in this case hydrate formation is likely to play a prominent part, since caustic soda is known to form comparatively stable solid hydrates, and is probably highly hydrated in solution (see Pickering, *Trans. Chem. Soc.*, 1895, 890). This effect stands in marked contrast to the action of ammonium salts, as shown in the accompanying table.



I. Added salt conc. = 0.4 N.	II. D.	III. Mean value of D.	IV. Pressure calculated for 1.0 N. $\text{NH}_3$ .	V. Alteration caused by salt.
$\text{NH}_4\text{Cl}$ . .	$\left\{ \begin{array}{l} 13.31 \\ 13.34 \\ 13.35 \\ 13.35 \end{array} \right\}$	13.34	13.54	+ 0.09
$\text{NH}_4\text{NO}_3$ . .	$\left\{ \begin{array}{l} 13.15 \\ 13.17 \end{array} \right\}$	13.16	13.43	- 0.02
$\text{NH}_4\text{I}$ . . .	$\left\{ \begin{array}{l} 12.92 \\ 12.85 \end{array} \right\}$	12.83	13.20	- 0.25
$\text{NH}_4\text{NCS}$ . .	$\left\{ \begin{array}{l} 12.83 \\ 12.82 \end{array} \right\}$	12.82	13.18	- 0.27

D represents the pressure found in millimetres of mercury. The solution was titrated at the end of the experiment, so as to avoid the error caused by loss of ammonia during the addition of the salt. The amount of ammonia removed by the gas during the experiment was negligible. The pressures which would have been produced by an exactly normal solution of ammonia were calculated and are given in Column IV.

Thus addition of ammonium ions does not cause an increase in the pressure of ammonia. Actually all the values must be a little too high, since the mass of water present per litre is less than in a 1.0 N. ammonia solution. The correction, as calculated by Gaus, amounts to 1.2-2.0 per cent. Thus it looks as if some chemical reaction occurs, either a complex ion of the type  $\text{NH}_4(\text{NH}_3)^+$  or a salt analogous to a hydrated salt, in which water is replaced by ammonia being formed. Gaus points out that these two views are practically identical, since it is certain that many ions in solution are hydrated, and such hydrates fall within the definition of complex ions.

A further series of measurements with ammonium salts of dibasic acids, however, showed that in this case the

behaviour is entirely different, as will be seen from the following table:—

Added salt 0·4 molar.	D.	Mean pressure calculated for 1·0 N. $\text{NH}_3$ .	Alteration.
<sup>1</sup> $\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$ . .	$\left\{ \begin{smallmatrix} 14\cdot10 \\ 14\cdot14 \end{smallmatrix} \right\}$	14·42	+ 0·97
<sup>1</sup> $\frac{1}{2}(\text{NH}_4)_2\text{C}_2\text{O}_4$ . .	$\left\{ \begin{smallmatrix} 13\cdot95 \\ 13\cdot97 \end{smallmatrix} \right\}$	14·27	+ 0·82
<sup>1</sup> $\frac{1}{2}(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ .	$\left\{ \begin{smallmatrix} 13\cdot70 \\ 13\cdot67 \end{smallmatrix} \right\}$	13·83	+ 0·38

The idea of attributing the increases of pressure caused by di-basic ammonium salts to hydrolysis may be summarily dismissed, as calculation from the known dissociation constants shows that it would be immeasurably small. Also the tartrate, as the salt of the weakest acid, should show the greatest increase in pressure, whilst it actually shows the smallest.

The divergence in behaviour between the mono- and dibasic ammonium salts cannot be explained on the grounds that the concentrations of the ammonium ions are greater in the case of dibasic salts, since the monobasic salts are much more highly dissociated than the dibasic ones.

Hantzsch and Sebaldt (*Zeit. phys. Chem.*, **30**, 258 (1899)) made measurements of the distribution coefficient of ammonia between water and chloroform in presence of ammonium chloride (in the water layer), and found that increasing the concentration of ammonium chloride did not alter the apparent distribution coefficient, in approximate agreement

<sup>1</sup> These concentrations are given in the original as 0·4 molar with respect to the complete salt molecule. In the complete table of the results at the end of the paper, however, the formula is written " $\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$ ," etc., and it seems probable that these solutions were 0·4 N. in common with all the others examined, especially in view of the comparison drawn by Gaus between these solutions and those of the monobasic ammonium salts.

with Gaus's results; and they obtained a similar result with piperidin, which is much more dissociated than ammonium hydroxide. On the other hand, addition of caustic soda caused an increase in the concentration of ammonia in the chloroform layer, also in agreement with Gaus's results. Unfortunately no experiments were made with dibasic ammonium salts.

Arrhenius (*Zeit. phys. Chem.*, 1 (1887)) found that addition of monobasic ammonium salts causes a considerable reduction in the speed of saponification of ethyl acetate by ammonia, while the reduction caused by addition of ammonium sulphate was much smaller. Parallel experiments with potassium, sodium and barium salts, and the corresponding hydroxides, showed an abnormality precisely similar to that shown by ammonium salts in the ammonia pressure experiments, the halides and the nitrate in each case reducing the speed of saponification, while the sulphates of potassium and sodium increased it—a fact for which no explanation has been offered.

Subsequent work by Abegg and Riesenfeld (*Zeit. phys. Chem.*, 40, 84 (1902)) on the effect of addition of salts of metals which do not readily yield complex ions (mainly alkali salts) to ammonia solutions upon the pressure of the latter showed that the anion plays a certain part in the effect.

The divergence in behaviour of the mono- and di-basic ammonium salts in ammonia solutions must be regarded as a puzzle.

Returning to Gaus's experiments, the results found by him are shown in the following table:—

## 1.0 N. AMMONIA SOLUTION.

Added salt.	Conc. $\frac{\text{mol.}}{\text{litre}}$	$\Delta D$ mm. mercury.	$\frac{\Delta D}{13.45} \div \text{conc.}$ of added salt.
NaOH . . .	0.4	+ 1.51	—
KCl . . .	0.4	+ 1.00	—
$\frac{1}{2}(\text{NH}_4)_2\text{SO}_4$ . . .	0.4	+ 0.97	—
$\frac{1}{2}(\text{NH}_4)_2\text{C}_2\text{O}_4$ . . .	0.4	+ 0.82	—
NaCl . . .	0.4	+ 0.79	—
$\frac{1}{2}(\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6$ . . .	0.4	+ 0.38	—
$\text{NH}_4\text{Cl}$ . . .	0.4	+ 0.09	—
$\text{NH}_4\text{NO}_3$ . . .	0.4	- 0.02	—
$\text{BaCl}_2$ . . .	0.4	- 0.02	—
$\text{NH}_4\text{I}$ . . .	0.4	- 0.25	—
$\text{NH}_4\text{NCS}$ . . .	0.4	- 0.27	—
$\text{SrCl}_2$ . . .	0.4	- 0.29	—
$\text{CaCl}_2$ . . .	0.4	- 0.77	—
$\text{MgCl}_2$ . . .	0.4	- 2.01	—
$\text{CuSO}_4$ . . .	0.0982	- 5.02	3.8
$\text{CuSO}_4$ . . .	0.0491	- 2.49	3.8
$\text{Cu}^1\text{Cl}$ . . .	0.02	- 0.44	1.6
$\text{AgCl}$ . . .	0.0491	- 1.39	2.1
$\text{ZnSO}_4$ . . .	0.01	- 0.44	3.3
$\text{CdSO}_4$ . . .	0.01	- 0.52	3.9

The figures in the last column show the number of ammonia molecules removed by each molecule of the added salt. The results with silver and copper thus agree well with those of other observers.

For an examination of solutions of  $\text{Cu}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Cd}(\text{OH})_2$ ,  $\text{Zn}(\text{OH})_2$ , and  $\text{Ag}_2\text{O}$  in ammonia, see Bonsdorff (*Zeit. anorg. Chem.*, **46**, 132 (1904)).

Similar experiments were made with sulphur dioxide by C. J. J. Fox (*Zeit. phys. Chem.*, **41**, 458 (1902)). Fox extended the use of Rothmund's (*loc. cit.*) formula for the solubility of a substance in water containing an indifferent salt, namely

$$\frac{1}{n} = \frac{l_0 - l}{l_0} = \text{const.},$$

where  $n$  = salt concentration,

$l_0$  = solubility of substance in water,

$l$  = solubility of substance in salt solution.

Now, if the heats of solution of the substance in water and in the salt solution respectively be  $q_0$  and  $q$ , we have

$$\frac{q_0}{2T^2} = \frac{d \log l_0}{dT}$$

and

$$\frac{q}{2T^2} = \frac{d \log l}{dT}$$

If  $q_0$  is not equal to  $q$ , the difference must be the heat effect of a chemical reaction between the salt and the substance dissolved. Calling this  $q_1$ , we have

$$q_0 - q = \frac{d \log \frac{l_0}{l}}{dT} \cdot 2T^2 = q_1$$

that is, if the ratio of the solubilities in water and in the salt solution changes with temperature, a thermochemical reaction must have occurred between the two solutes.

The absorption coefficient of sulphur dioxide was measured in solutions of twelve salts at  $25^\circ$  and at  $35^\circ$ , and in each case the values of  $\frac{1}{n} \cdot \frac{l_0 - l}{l_0}$  showed a temperature coefficient, excepting the cases of the three salts, ammonium sulphate, sodium sulphate, and cadmium sulphate, thus indicating a reaction between gas and solute.

The absorption coefficient was also measured at  $25^\circ$  in solutions of various strengths of the following salts: KI, KNCS, KBr, KCl,  $\text{KNO}_3$ ,  $(\text{NH}_4)_2\text{SO}_4$ . In each case the measurements were carried out at two pressures of sulphur dioxide, namely, 760 mm. and 77.93 mm., the sulphur dioxide in the latter case being diluted with carbon dioxide. The accompanying table shows the value of the expression

$$\frac{1}{p \cdot n} \cdot \frac{l - l_0}{l_0}$$

at  $25^\circ$ ,  $p$  being the pressure of sulphur dioxide. The expression has a constant value for each salt, showing that the quantity of sulphur dioxide which combines with the salt is proportional to the first power of  $p$ . The change in the absorption coefficient is also proportional to  $n$ , so that in

each case the formula of the complex salt formed (if any) must be

one molecule salt : one molecule sulphur dioxide.

The conductivities of solutions of many salts alone on the one hand, and saturated with sulphur dioxide on the other, were also measured. In weak salt solutions addition of sulphur dioxide caused an increase in conductivity, as was to be anticipated from the fact that sulphurous acid is formed. Plotting the conductivities as ordinates against salt concentrations as abscissæ, however, we find that the conductivity of salt solutions saturated with sulphur dioxide rises more slowly than that of the salt solutions alone, and in many cases the two curves cut one another at about 2.0 N. In these cases a slow-moving complex ion must have been formed.

Salt.	Pressure of SO <sub>2</sub> .	Salt concentration.					
		3 N.	2.5 N.	2.0 N.	1.5 N.	1.0 N.	0.5 N.
KI . . .	{ 760 mm.	0.00476	0.00480	0.00481	0.00478	0.00482	0.00461
	{ 77.93 mm.	0.00464	0.00451	0.00465	0.00465	0.00477	0.00471
KNCS . .	{ 760 mm.	0.00380	0.00371	0.00383	0.00382	0.00387	0.00387
	{ 77.93 mm.	0.00385	0.00384	0.00377	0.00376	0.00379	0.00385
KBr . . .	{ 760 mm.	0.00254	0.00252	0.00255	0.00245	0.00256	0.00255
	{ 77.93 mm.	0.00245	0.00248	0.00252	0.00243	0.00245	0.00269
KCl . . .	{ 760 mm.	0.00127	0.00131	0.00131	0.00134	0.00128	0.00133
	{ 77.93 mm.	0.00135	0.00129	0.00135	0.00139	0.00130	0.00136
<sup>1</sup> KNO <sub>3</sub> . .	{ 760 mm.	0.00077	0.000773	0.000761	0.000786	0.000814	0.000834
	{ 77.93 mm.	0.000802	0.000801	0.000826	0.000781	0.000768	0.000774
<sup>1</sup> $\frac{1}{2}$ (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	{ 760 mm.	0.000428	0.000436	0.000440	0.000424	0.000426	0.000474
	{ 77.93 mm.	0.000427	0.000434	0.000423	0.000423	0.000422	0.000427

Finally it was found possible in several cases to isolate solid compounds of sulphur dioxide with salts. The

<sup>1</sup> The figures given for these salts in the original paper were all (save the first) 10 times as great as those recalculated from the experimental data. The figures given are therefore all recalculated.

powdered solid salt was moistened with a little water, and a stream of dry sulphur dioxide was passed over the mixture until it became dry. The tube containing the solid was now weighed, and warmed until all the sulphur dioxide was driven off. On weighing again, the weight was found to be that of the tube and the original quantity of salt. Thus the amount of sulphur dioxide absorbed was determined. In the cases of KI, KBr, KCl, and KNCS, the weights of sulphur dioxide absorbed were 95, 90, 91, and 93 per cent. respectively of the quantity required for complete formation of the compound  $KXSO_2$ , where X represents the acid radical. Potassium nitrate showed no absorption at all, so that although the compound  $KNO_3SO_2$  can probably exist, it must have a pressure of more than 760 mm. of sulphur dioxide at the ordinary temperature.

Walden and Centnerszwer (*Zeit. phys. Chem.*, **42**, 432 (1902)) succeeded in preparing and analysing the solid compound  $KI_4SO_2$ . Freezing-point experiments appeared to show the presence of  $KI_4SO_2$  and  $KI(13-16)SO_2$  in solution. The latter compound was also separated in a more or less pure condition. Analysis showed it to contain (1) 15·8, (2) 14·6, (3) 15·2 molecules of sulphur dioxide for each molecule of potassium iodide.

## CHAPTER IX

### SOME COBALT AND COPPER SOLUTIONS

#### A. The Cobalt and Cupric Halides.

A solution of cobalt chloride in water has a decided red colour, but addition of certain chlorides, such as hydrochloric acid, magnesium chloride or calcium chloride, causes the colour to change from red to blue.

If the blue colour is due to formation of a complex ion, such as  $\text{CoCl}_3'$  or  $\text{CoCl}_4''$ , we should expect to find that on passing a current through a cell having its kathode immersed in the blue solution and its anode in a colourless electrolyte, a blue colour-boundary would move from the kathode towards the anode.

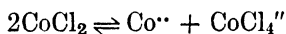
The experiment was made by Donnan and Bassett (*Trans. Chem. Soc.*, 1902, 939). Two vessels were filled with the blue solution of cobalt and calcium chlorides and connected by a tube containing pure calcium chloride solution. On passing a current through the cell a blue colour-boundary entered the tube from the kathode end and travelled towards the anode, while no colour appeared in the tube at the anode end.

On the other hand, if the two end vessels were filled with red cobalt chloride solution whilst the connecting tube contained a solution of potassium chloride, a pink layer entered the tube from the anode vessel, and travelled towards the kathode, and no colour-boundary entered the tube from the kathode vessel.

Again, an alcoholic solution of cobalt chloride conducts electricity freely, while the apparent molecular weight of the salt as determined by the boiling point is a little higher



than the normal, viz. 140 instead of 130. Donnan and Bassett pointed out that if the salt ionised according to the scheme



the solution would conduct electricity although the apparent molecular weight would remain normal. They also quoted the following evidence for the existence of complex anions containing cobalt :—

### 1. *Solubility.*

Sabatier (*Comptes Rendus*, **107**, 42) showed that the solubility of cobalt chloride in water is first diminished and then increased by continuous addition of hydrochloric acid.

### 2. *Conductivity.*

Trötsch (*Ann. der Physik und Chemie*, **41**, 259 (1890)) found that the temperature-coefficient of the conductivity of strong solutions of cobalt chloride at first increases with rise in temperature and then diminishes. There is a point of inflexion in the conductivity-temperature curve between 40° and 50°, beyond which the temperature coefficient is negative. Similar points of inflexion are shown by cupric chloride and some sulphates, while all binary electrolytes examined, such as chlorides, nitrates, chlorates, etc., of the alkali metals show continually increasing temperature-coefficients.

### 3. *Transport Numbers.*

Bein (*Zeit. phys. Chem.*, **27**, 1 (1898)) found that the transport number for cobalt in cobalt chloride solutions decreases as the concentration rises. The experiments were carried out at different temperatures, however, so that this evidence is of somewhat doubtful value.

### 4. *Heat of Dilution.*

The fact that the temperature-coefficient of the conductivity falls with rise of temperature and ultimately becomes negative shows that the reaction which lowers the conductivity is favoured by rise of temperature and is therefore endothermic. This reaction is probably the formation of complex ions, since simple electrolytic dissociation usually

increases very fast with rise of temperature. If this is the case, heat should be evolved on diluting the solution, owing to the dissociation of the endothermic complex salt. Experiment shows that this is the case.

Donnan and Bassett therefore concluded that the blue colour was due to the complex ion  $\text{CoCl}_3'$  or  $\text{CoCl}_4''$ :  $\text{CoCl}_2$  was probably blue,  $\text{Co}^{++}$  was red.

Biltz (*Zeit. phys. Chem.*, **40**, 198 (1902)) showed that cobalt chloride and cupric chloride and bromide have unusually big freezing-point depressions in water solution, presenting a marked contrast to the boiling point of cobalt chloride solutions in alcohol. This would agree with Donnan and Bassett's theory, however, that complex formation is small at low temperatures and large at high ones.

Kohlschutter (*Ber.*, **37**, 1, 1153 (1900)) carried out migration experiments with cupric chloride solutions, and concluded that there was no doubt as to the formation of complex ions in them.

G. N. Lewis (*Zeit. phys. Chem.*, **52**, 222, and **56**, 223) observed the colours produced by adding cupric bromide to 3 M. solutions of a large number of salts. The colours varied from blue to green except in the case of other bromides, when brown solutions were formed. Cupric chloride gave a green colour in chloride solutions, and blue in all others. Cobalt chloride was red in all solutions save those of chlorides, when it had a bluish tint.

Lewis concluded that the colour changes were due to change in the degree of hydration, but the evidence for this appears somewhat weak. It is significant that special results were produced in each case by salts having a common ion.

Benrath (*Zeit. anorg. Chem.*, **54**, 328 (1907)) found that certain chlorides, such as mercuric, zinc, cadmium and stannous chlorides, instead of producing a blue colour in solutions of cobalt chloride, hinder its production. Measurements of the boiling points of aqueous solutions of these salts in presence of cobalt chloride showed that the rise was much

smaller than was to be expected under ordinary conditions of dissociation, and it was therefore to be assumed that complex-formation had occurred. Experiments with barium, calcium, sodium, magnesium, aluminium and hydrogen chlorides showed that with these salts the rise in the boiling point was normal. These are the salts that increase the blue colour. Donnan and Bassett's theory was therefore called into question.

Denham (*Zeit. phys. Chem.*, **65**, 641) next studied the subject and measured the migration ratio in solutions of cupric chloride and bromide and of cobalt bromide. As the concentration increases, the migration ratio for the kation becomes continually less. Unless very abnormal changes in the degree of hydration are assumed to occur, this must necessarily be due to the formation of complex anions, probably of the type  $\text{CoCl}_3'$  or  $\text{CoCl}_4''$ . The changes in colour are approximately parallel to the changes in the constitution of the solution on this hypothesis.

Further, in reply to Benrath, it was pointed out that while addition of a salt such as calcium or magnesium chloride will obviously cause a large increase in the amount of complex ions formed, addition of a salt having a stronger tendency to form complex ions or undissociated salts, such as mercuric or cadmium chloride, will cause a diminution in the amount of cobalt complex present.

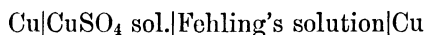
This theory appears to offer a fairly complete account of the facts. At the same time, the fact that calcium and magnesium chlorides show a greater tendency to cause formation of the blue colour than the alkali chlorides seems to indicate that the high degree of hydration which these salts probably possess in solution favours formation of the complex ion containing cobalt by reducing the active mass of water in the solution, so that both hydrate- and complex-formation perhaps play a part in the phenomena.

Jones (*Zeit. phys. Chem.*, **74**, 358 (1910)) is of opinion that the colour changes are caused by change in the degree of hydration.

**B. Fehling's Solution, etc.**

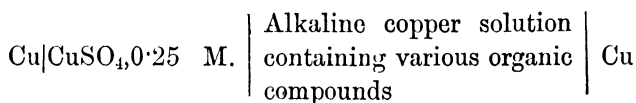
Another class of solutions which contain copper in an abnormal condition is that in which copper oxide is dissolved by various organic acids and strongly hydroxylated compounds in alkaline solution, as, for example, in Fehling's solution. In these solutions the copper may not be complex in the sense of our definition, as it is quite probable that only the usually-accepted valencies are exercised, but it may be of interest to add some account of such solutions.

Kahlenberg (*Zeit. phys. Chem.*, **17**, 586 (1895)) measured the potential of the cell



The values found showed that only minimal amounts of copper ions were present in the Fehling's solution. The depression of the freezing point shown by Fehling's solution was also smaller than that calculated from the separate ingredients.

The potentials of a series of cells of the type



were also measured, the organic compounds used being glycollic acid, lactic acid, malic acid, citric acid, glycerol, erythrose, mannose, cane sugar and biuret. In each case a large potential (0.2–0.5 volt) was produced, showing that the copper ion concentration in the alkaline solution was exceedingly small.

A more thorough investigation of Fehling's solution was carried out by Masson and Steele (*Trans. Chem. Soc.*, 1899, 725). Pure cupric tartrate was shaken with caustic potash solution, addition of potash being continued until the precipitate was nearly all dissolved, care being taken that some remained. On filtering the mixture, a clear deep blue solution was obtained which was perfectly neutral.

Two flasks with side necks were connected by a glass

tube of narrow bore filled with a solid solution which was 1.0 N. with respect to sodium chloride and contained 12 per cent. of gelatine. Platinum electrodes were placed in the flasks, both of which were filled with the deep blue solution. The apparatus was placed in cold water and an E.M.F. applied to the electrodes. Deep blue anions moved away from the kathode through the tube, while the kations were evidently colourless. The kathode became plated with copper, evidently as the result of a secondary reaction following upon the discharge of potassium ions. In another experiment the anode vessel was filled with copper sulphate solution, while the kathode vessel contained the deep blue solution as before. Two blue boundaries now appeared on passing the current, a deep blue one from the kathode end and a pale blue one from the anode end.

Similar experiments were also made by Küster (*Zeit. Elektrochemie*, 4, 105).

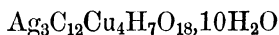
Masson and Steele now substituted a graduated tube for the plain one, in order to measure the velocities of the two coloured ions. As the electrolysis proceeded, however, it was found that the ratio of the two velocities did not remain constant; and the light blue boundary suddenly formed a pale blue precipitate at a certain definite point in the tube, where it had been expected that the two boundaries would meet, while the dark blue one was still some distance away. The dark blue solution must therefore contain a faster colourless ion together with the dark blue one, which is capable of giving a precipitate with cupric ions. This is probably the tartrate ion, and the solution must contain some potassium tartrate.

Next, the amount of alkali required for production of the neutral deep blue solution was determined by titrating a weighed quantity of cupric tartrate, the alkali being added until the salt just dissolved and the resulting solution being tested with litmus. It was ascertained in this way that the ratio  $\text{NaOH} : \text{CuC}_4\text{H}_4\text{O}_6$  is almost exactly 1.25 : 1, or, in whole numbers, 5 : 4.

Masson and Steele considered the reaction to be probably represented by the equation



and the correctness of this was tested as follows. On adding alcohol to the solution a crystalline blue precipitate is thrown down, leaving the liquid colourless. The liquid proved to contain alkali tartrate in about the quantity required by the above equation. Analysis of the precipitate showed that its composition agrees with the formula  $\text{K}_3\text{C}_{12}\text{Cu}_4\text{H}_7\text{O}_{18}, 5\text{H}_2\text{O}$ . Whether all the water is present as water of crystallisation is uncertain. From a solution of this compound the silver salt was precipitated, amongst others, and analysis of it gave results agreeing with the formula



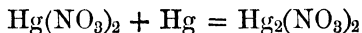
Little is known of the stability of the ion,  $\text{C}_{12}\text{Cu}_4\text{H}_7\text{O}_{18}'''$ , which is probably produced, save that it does not yield cupric hydroxide with caustic alkali, but does give copper sulphide on treatment with hydrogen sulphide.

## CHAPTER X

### SOME SPECIAL CASES OF EQUILIBRIUM

#### A. Equilibrium between Metals in Different Stages of Oxidation.

If a metal forms two series of salts, there must be an equilibrium in the system containing the metal and its two ions. Thus, if we place a solution of mercuric nitrate over mercury, the reaction



occurs to a considerable extent. The presence of mercurous nitrate in the liquid can be readily proved by adding potassium chloride when calomel is precipitated.

We know from thermodynamic considerations, however, that no reaction can proceed to absolute completion, and accordingly the present one must be regarded as leading to a condition of equilibrium. Assuming that both salts are equally ionised, which is sufficiently near the truth, the reaction in the solution may be represented by the equation



Since liquid mercury is present, its concentration is constant, and the condition of equilibrium is given by the equation

$$[\text{Hg}^{++}] = k[\text{Hg}_2^{++}]$$

For the sake of clearness in the example we have anticipated the proof of the constitution of the mercurous ion.

From the above equation for the reversible reaction we may draw the important general conclusion that a salt

corresponding to the highest stage of oxidation of a metal can exist in the pure state—subject to its dissociation into metal and non-metal—in absence of the free metal; while salts corresponding to lower stages of oxidation cannot exist at all in the pure state (saving in the metastable condition, such as, for example, the state of solid calomel) since they spontaneously decompose to some extent into the metal and a salt corresponding to a higher stage of oxidation. Thus Behrend (*Zeit. phys. Chem.*, **11**, 474 (1893)) found that mercurous iodide decomposed on solution in water into mercury and mercuric iodide. This decomposition was further studied by Ogg (*Zeit. phys. Chem.*, **27**, 285 (1898)). The decomposition of calomel into mercury and mercuric chloride was referred to by Richards (*Zeit. phys. Chem.*, **24**, 39).

A very thorough study of the equilibria



and



was made by Abel (*Zeit. anorg. Chem.*, **26**, 361 (1901)).

Abel's first experiments were made with a view to ascertaining the value of the equilibrium constant for the reaction



which is given by  $k = \frac{[\text{Hg}_2^{++}]}{[\text{Hg}^{++}]}$

A solution of mercuric nitrate in ca. 0.3 N. nitric acid was shaken with mercury in a thermostat in an atmosphere of carbon dioxide. A portion of the resulting solution was pipetted out and the mercurous mercury precipitated with potassium chloride and weighed. The filtrate was treated with hypophosphorous acid, which reduced the mercuric mercury to the mercurous condition, so that a further quantity of calomel was precipitated. This was also weighed. The following table shows the results obtained at 25°:—



$\text{HgNO}_3$ conc.	$\text{Hg}(\text{NO}_3)_2$ conc.	$k = \frac{[\text{HgNO}_3]}{[\text{Hg}(\text{NO}_3)_2]}$	$k' = \frac{[\text{HgNO}_3]^2}{[\text{Hg}(\text{NO}_3)_2]}$
0.05163	0.000216	239.03	12.3
0.10042	0.000419	239.7	24.2
0.11059	0.000461	239.9	26.5

The concentrations are the total mercurous and mercuric contents respectively, calculated in terms of the formulæ  $\text{HgNO}_3$  and  $\text{Hg}(\text{NO}_3)_2$ . Thus the degrees of dissociation are taken as equal. The fact that the ratio  $\frac{[\text{HgNO}_3]}{[\text{Hg}(\text{NO}_3)_2]}$  is constant shows that the mercurous ion consists of two mercury atoms.  $k'$  corresponds to the formula  $\text{Hg}'$  for the mercurous ion, as will be evident from the scheme



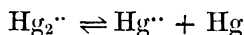
Thus the mercurous ion has the formula  $\text{Hg}_2^{..}$  and the constant

$$k = \frac{[\text{Hg}_2^{..}]}{[\text{Hg}']}$$

has the value 120 very nearly.

Abegg and Shukoff (*Zeit. für Elektrochemie*, **12** (1906)) showed that a mercury anode dissolves in these proportions.

We are now in a position to explain several remarkable facts relating to the behaviour of mercury salts. Thus, since



it follows that if mercuric ions be removed from a solution containing mercurous and mercuric ions in equilibrium with mercury, more mercurous ions will dissociate, producing a further supply of mercuric ions and free mercury. Thus, if we add potassium cyanide to a solution of mercurous nitrate the mercuric ions present will form mercuric cyanide which is practically undissociated, and the  $\text{Hg}'$  concentration will become very small. This will cause nearly complete dissociation of the mercurous ions, so that the substances react almost completely so as to produce mercuric cyanide, potassium nitrate, and mercury.

Similarly we can understand how addition of a chloride to calomel causes precipitation of mercury. The foreign chloride ions cause a large depression in the (already very small) concentration of mercuric ions, and this causes the mercurous ions to split up. A similar result is produced by the addition of sodium nitrite to mercurous nitrate, the mercuric ions being removed in this case to form the complex ion  $\text{Hg}(\text{NO}_2)_4^{--}$  (Pick, *loc. cit.*). In general, then, the addition to a mercurous salt in solution of any substance which removes mercuric ions promotes its decomposition.

Again, we can throw a general light upon the behaviour of mercurous salts with hydrogen sulphide. Since addition of sulphur ions to a mercurous solution causes precipitation of mercuric sulphide and mercury, we have in the solution mercuric ions in equilibrium with mercury, and therefore also with mercurous ions. Hence, if the two substances were precipitated together, we should have the relation

$$\begin{aligned}\frac{[\text{Hg}_2^{++}]}{[\text{Hg}^{++}]} &= \frac{[\text{Hg}_2^{++}][\text{S}^{--}]}{[\text{Hg}^{++}][\text{S}^{--}]} = \frac{L_{\text{Hg}_2\text{S}}}{L_{\text{HgS}}} \\ &= \frac{(\text{solubility of mercurous sulphide})^2}{(\text{solubility of mercuric sulphide})^2} = 120\end{aligned}$$

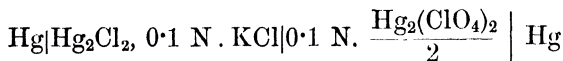
Thus, if the solubility of mercuric sulphide were  $\frac{1}{11}$ th of that of mercurous sulphide, the two sulphides would be precipitated together, *i.e.*  $25^\circ$  would be the transition temperature in the system



The fact that only mercuric sulphide and mercury are precipitated shows that the solubility of mercuric sulphide is less than  $\frac{1}{11}$ th of that of mercurous sulphide, and that mercurous sulphide is therefore unstable, and would spontaneously decompose into mercuric sulphide and mercury.

The determination of the constant  $\frac{[\text{Hg}_2^{++}]}{[\text{Hg}^{++}]}$  is also important in relation to the calomel electrode. A calculation of the concentrations of mercurous and mercuric ions in the

normal calomel electrode, based upon various measurements by other observers, was given by Sherill (*Zeit. phys. Chem.*, **43**, 711 (1903)). Later the subject was specially studied by Ley and Heimbucher (*Zeit. für Elektrochemie*, **10**, 301 (1904)), who measured the E.M.F. of the cell



In order to ascertain the degree of dissociation of the mercurous perchlorate, a series of measurements of its conductivity was made. A correction was applied for the hydrolysis which the salt undergoes in solution, the concentration of free perchloric acid being measured by determining the rate of hydrolysis of cane sugar in a solution of the salt. (Unfortunately the calculation as printed in the original paper contains a misprint.)

On the assumption that the hydrolysis is represented by the scheme



Ley and Heimbucher calculated that a 0.1 *N.* solution of mercurous perchlorate contains 0.047 *gram molecule* of unhydrolysed salt, and is 0.035 *M.* with respect to mercurous ions. The correction for hydrolysis is small, and if the scheme shown above does not represent the reaction, the error cannot be great.

The two electrode vessels were connected through a solution of potassium nitrate with a view to minimising the liquid potential.

Thus it was found that the concentrations of mercurous ions in the decinormal electrode and in the normal one are respectively  $2.0 \times 10^{-16}$  and  $3.5 \times 10^{-18}$ .<sup>1</sup> Hence the

<sup>1</sup> From these figures Ley and Heimbucher calculated the solubility of calomel. Calling the solubility product *L*, and the solubility in water *s*, we have

$$4s^3 = L = [\text{Hg}_2^{++}][\text{Cl}']^2 = 2.0 \times 10^{-16}(0.086)^2$$

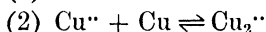
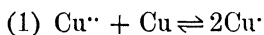
for the decinormal electrode, and similarly,

$$4s^3 = 3.5 \times 10^{-18}(0.75)^2$$

for the normal electrode. These equations give  $s = 0.72 \times 10^{-6}$  and  $s = 0.79 \times 10^{-6}$  *gram molecules* per litre respectively.

concentrations of the mercuric ions are  $1.7 \times 10^{-18}$  and  $3.1 \times 10^{-20}$ .

Abel (*loc. cit.*) also studied the equilibrium existing between cuprous ions on the one hand and cupric ions and copper on the other. The reaction is probably represented by one of the two following schemes:—



corresponding to which we obtain the constants

$$k = \frac{[\text{Cu}^{\cdot}]}{[\text{Cu}^{\cdot\cdot}]^2} \quad (1) \text{ and } k' = \frac{[\text{Cu}^{\cdot}]}{[\text{Cu}_2^{\cdot\cdot}]} \quad (2)$$

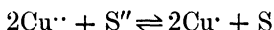
The equilibrium is thus independent of the anion, and in cases where this does not appear to be so, we have reason to believe that the disturbance is caused by complex formation. Thus, cupric chloride in acid solution in contact with copper gives a colourless solution in which no cupric ions can be recognised, while copper sulphate under the same conditions shows little change. Hence we may consider it probable that in the chloride solution a far-reaching complex formation has occurred in which the cuprous ion takes part, thus causing practically all the cupric ions to become reduced. This complex-formation was subsequently recognised and investigated by Bodländer and Storbeck (*Zeit. anorg. Chem.*, **31** (1902), pp. 1, 458).

Abel found that complex-formation also occurs in the sulphate solution, and the investigation of the cupro-cupric equilibrium proved to be a matter of extreme difficulty. The constitution of the cuprous ion is still uncertain. For details of the subject the reader is referred to the original papers.

One other point of interest may be referred to in connection with the subject.

In contrast with the behaviour of mercury, a solution containing either cuprous or cupric ions yields when treated with hydrogen sulphide a precipitate consisting of cuprous and cupric sulphides *together*. Thus the transition point for

the system cupric sulphide, cuprous sulphide, and sulphur lies at about the ordinary temperature. We may represent the reaction provisionally by the following equation :—



which gives the equilibrium constant

$$k = \frac{[\text{Cu}^{\cdot\cdot}]^2[\text{S}'']}{[\text{Cu}^{\cdot}]^2} = \frac{[\text{Cu}^{\cdot\cdot}]^2[\text{S}'']^2}{[\text{Cu}^{\cdot}]^2[\text{S}']^2}$$

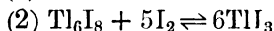
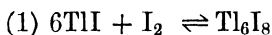
This gives the special relation

$$k = \frac{L_{\text{CuS}}^2}{L_{\text{Cu}_2\text{S}}}$$

since the solution is saturated with respect to both sulphides. The last equation holds good whether we take the formula of the cuprous ion as  $\text{Cu}^{\cdot}$  or  $\text{Cu}_2^{\cdot\cdot}$ , providing the proper dimensions are given to  $L$ .

A further interesting case of equilibrium between salts corresponding to different stages of oxydation of a metal is that of the iodides of thallium. This was exhaustively studied by Abegg and Maitland (*Zeit. anorg. Chem.*, **49**, 341 (1906)).

When shaken with solutions of iodine in carbon disulphide, carbon tetrachloride or aqueous potassium iodide, thallous iodide takes up iodine, yielding one of two solid products according to the concentration of iodine. These two solid products are (1)  $\text{Tl}_6\text{I}_8$  and (2)  $\text{TlI}_3$ . The transition iodine pressure at  $25^\circ$  was determined for the two reactions



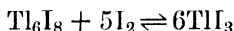
In the case of the non-aqueous solvents, the corresponding concentration of aqueous iodine is obtained by multiplying the experimentally found value by the distribution coefficient.

Thus a large quantity of thallous iodide was shaken for seven days at  $25^\circ$  with a solution of iodine in carbon disulphide containing initially 32.5 millimolecules of iodine per litre. After shaking, the titre was found to have fallen to 4.475 millimolecules per litre. The carbon disulphide

solution was now diluted slightly, and the shaking continued for seven days more. At the end of this time the titre was again 4.475 millimolecules per litre, so that iodine had separated out from the solid phase until this concentration was reached in the solution. This is therefore the concentration corresponding to equilibrium between the solids  $\text{TlI}$  and  $\text{Tl}_6\text{I}_8$ . Multiplying the iodine concentration by the distribution coefficient,  $\frac{1}{590}$ , we obtain for aqueous solution the equilibrium concentration

$$\frac{4.475}{590 \times 1000} = 0.76 \times 10^{-5} \text{ mols. per litre of water.}$$

In accordance with this result, the solid  $\text{Tl}_6\text{I}_8$  was obtained by treating thallos iodide with a solution of iodine in aqueous potassium iodide. Starting with this body and carbon disulphide, the same iodine titre as before was obtained, showing that the solid oxydation product in the previous experiment was really  $\text{Tl}_6\text{I}_8$ . In a similar manner it was shown, using carbon tetrachloride solutions, that the equilibrium concentration in water for the reaction



is  $3.3 \times 10^{-4}$  gram molecules per litre.

In order to ascertain whether  $\text{TlI}_3$  was the highest oxydation product, solid  $\text{TlI}_3$  was shaken with a saturated solution of iodine in carbon tetrachloride. The concentration of the solution remained unaltered, showing that the system  $\text{TlI}_3 + \text{I}_2$  is stable, and  $\text{TlI}_3$  is the highest iodide that exists at  $25^\circ$ .

The latter compound may, theoretically, be either of two possible isomerides, namely, thallos triiodide,  $\text{TlI}_3$ , corresponding to the triiodides of the alkali metals, and yielding the complex ion  $\text{I}_3'$ , or thallic iodide, yielding the ions  $\text{Tl}^{+++}$  and  $3\text{I}'$ .

A series of experiments showed that in solution this substance exists simultaneously in both forms, so that it is apparently an example of inorganic tautomerism. From its small solubility, and the fact that it is isomorphous with

caesium triiodide (Wells and Penfield, *Zeit. anorg. Chem.*, **6**, 312 (1894)), it appears probable that the solid is thalious triiodide.

When thalious iodide is shaken with iodine and potassium iodide, a certain amount of thallium goes into solution. Both alkali iodide and iodine play an essential part in this reaction, which is thus to be regarded as caused by the formation of a *complex thallic* ion. In the following calculations the formula  $\text{TlI}_4'$  is assigned to this ion, and the results show that the formula is the correct one.

Solutions of potassium iodide of various concentrations (Column II.) were shaken with thalious iodide and iodine at 25°. The iodine enters into three reactions, viz. (1) it combines with the  $\text{I}'$  ions produced by the potassium iodide, forming the complex ion  $\text{I}_3'$  in the manner found by Jakowkin. We may call this portion, for convenience, "Jakowkin iodine." (2) Another portion of the iodine converts the thalious iodide into one of the solids  $\text{Tl}_6\text{I}_8$  or  $\text{TlI}_3$ . (3) A further portion of the iodine enters into combination with thallium in solution forming the complex ion  $\text{TlI}_4'$ . Finally the remaining iodine exists in solution in the free state.

The concentration of this free iodine (Column V.) was determined by shaking the liquid with carbon tetrachloride or carbon disulphide. This, as we have already seen, determines the composition of the solid phase (Column III.).

The oxydation potential of the solution was measured against the 1.0 N. calomel electrode. This gives the concentration of the  $\text{I}'$  ions, since the oxydation potential,  $e_0$ , in the equation

$$e = e_0 + 0.059 \log_{10} \frac{\sqrt{[\text{I}_2]}}{[\text{I}']}$$

had been previously determined by Maitland (*Zeit. für Elektrochemie*, **12**, 263 (1906)). Its value, putting the E.M.F. of the 1.0 N. calomel electrode equal to 0, is +0.341 volt, whence

$$e = 0.341 + 0.059 \log_{10} \frac{\sqrt{[\text{I}_2]}}{[\text{I}]}$$

Thus in a solution in which the free iodine concentration has been determined by distribution we can calculate  $[I']$ . The values thus obtained are given in Column VIII. These values must be equal to the total concentration of potassium iodide, less the concentration of the iodine ions that have combined with iodine to form the ion  $I_3'$ , and the iodine ions that have combined with  $TII_3$  to form the complex ion  $TII_4'$ .

The iodine ( $I_2$ ) concentration found by titration (Column IV.) consists of the free iodine, the "Jakowkin" iodine and the iodine which separates from the neutral part ( $TII_3$ ) of the complex ion  $TII_4'$ . The concentration of free iodine may be neglected compared with the last two concentrations, so that the  $I_2$ -titre is practically equal to the concentration  $[I_3']$  plus the concentration  $[TII_4']$ . Each of these last two terms contains one iodine ion which has been taken from the original potassium iodide, and hence the difference between the original concentration of potassium iodide (Column II.) and the  $I_2$ -titre gives us the remaining free potassium iodide concentration. Multiplying this by the degree of dissociation taken from conductivity data for potassium iodide solutions, we obtain the concentration of iodine ions (Column IX.) which should agree with the value in Column VIII. In order to obtain the value of the degree of dissociation,  $\alpha$ , the concentration was taken as that of the total potassium in the solution ( $KI + KI_3 + KTII_4$ ), the error thus introduced being quite inconsiderable. The agreement between the values in Columns VIII. and IX. is quite good, and thus affords evidence for the correctness of the hypothetical formula  $TII_4'$  for the complex ion.

Further, the value of the constant

$$k_j = \frac{[I_2][I']}{[I_3']}$$

was calculated as follows. The concentration  $[I_2]$  is known from the distribution experiments (Column V.).  $[I']$  is obtained by subtracting the  $I_2$ -titre (Column IV.) from the



I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.
No.	Conc. of KI in solvent.	Solid phase.	Iodine titre, per I <sub>2</sub> -mole, per litre.	Free iodine, Mols. per litre.	Thallium in solution, Atoms per litre.	E.M.F. against 1.0 N calomel electrode = e.	[I] calc. from e.	$[U] = II - (I_2)$ + $(TlI_3)$	$k_f = \frac{[I_2][I]}{[I_2]}$	$\log \frac{[I]}{[I]}$	$\log [I]$	$\log [Tl...]$	$k_f'$ VI, XIII, VIII, c.	$k_m$ VI, VIII, [TlI <sub>3</sub> ]	$k \cdot \frac{XV}{[TlI]}$	$\frac{X}{[TlI]^{1/2} \cdot [V]}$
2.05		TlI, Tl <sub>2</sub> I <sub>3</sub>	0.0136	0.76. 10 <sup>-5</sup>	0.01066	0.2165	0.35	0.39	1.25. 10 <sup>-3</sup>	+ 23.68	-6.78	-30.46		3.05. 10 <sup>-2</sup>	4.0. 10 <sup>3</sup>	
5.05		Tl <sub>2</sub> I <sub>3</sub>	0.0421	2.9. 10 <sup>-5</sup>	0.03216	0.2330	0.36	0.37	1.34. 10 <sup>-3</sup>	23.12	-6.89	-30.01		0.894. 10 <sup>-1</sup>	3.1. 10 <sup>3</sup>	
9.05		Tl <sub>2</sub> I <sub>3</sub>	0.0861	0.647. 10 <sup>-4</sup>	0.0650	0.2451	0.34	0.33	1.27. 10 <sup>-3</sup>	22.71	-6.89	-29.60		1.91. 10 <sup>-1</sup>	3.0. 10 <sup>3</sup>	
10.05		Tl <sub>2</sub> I <sub>3</sub>	0.2450	2.49. 10 <sup>-4</sup>	0.1824	0.2740	0.2150	0.205	1.01. 10 <sup>-3</sup>	21.73	-6.63	-28.86		0.848	3.4. 10 <sup>3</sup>	
11.05		Tl <sub>2</sub> I <sub>3</sub> , TlI <sub>3</sub>	0.2844	3.3. 10 <sup>-4</sup>	0.2102	0.2805	0.1920	0.17	0.96. 10 <sup>-3</sup>	21.51	-6.59	-28.10		1.094	3.3. 10 <sup>3</sup>	1.8. 10 <sup>-8</sup>
12.05		TlI <sub>3</sub>	0.2950	4.56. 10 <sup>-4</sup>	0.1990	0.2855	0.1860	0.165	0.98. 10 <sup>-3</sup>	21.33	-6.74	-28.07		1.07	2.4. 10 <sup>3</sup>	1.7. 10 <sup>-8</sup>
13.05		TlI <sub>3</sub>	0.3324	0.755. 10 <sup>-3</sup>	0.1840	0.2955	0.16	0.135	0.85. 10 <sup>-3</sup>	21.00	-6.84	-27.84		1.15	1.5. 10 <sup>3</sup>	1.9. 10 <sup>-8</sup>
14.05		TlI <sub>3</sub> , I <sub>2</sub>	0.3588	1.36. 10 <sup>-3</sup>	0.1461	0.3090	0.1250	0.12	0.89. 10 <sup>-3</sup>	20.54	-6.97	-27.51		1.168	0.86. 10 <sup>3</sup>	2.0. 10 <sup>-8</sup>
1.025		TlI, Tl <sub>2</sub> I <sub>3</sub>	0.00705	0.76. 10 <sup>-5</sup>	0.00556	0.2320	0.1930	0.20	1.24. 10 <sup>-3</sup>	23.15	-6.52	-29.67	1.880. 10 <sup>30</sup>	2.92. 10 <sup>-2</sup>	3.8. 10 <sup>3</sup>	
2.05		"	0.0136	0.76. 10 <sup>-5</sup>	0.01066	0.2165	0.35	0.39	1.25. 10 <sup>-3</sup>	23.68	-6.78	-30.46	2.044. 10 <sup>30</sup>	3.05. 10 <sup>-2</sup>	4.0. 10 <sup>3</sup>	
3.10		"	0.0275	0.76. 10 <sup>-5</sup>	0.02154	0.1975	0.74	0.76	1.24. 10 <sup>-3</sup>	24.32	-7.105	-31.425	1.914. 10 <sup>30</sup>	2.91. 10 <sup>-2</sup>	3.8. 10 <sup>3</sup>	
2.05		TlI, Tl <sub>2</sub> I <sub>3</sub>	0.0136	0.76. 10 <sup>-5</sup>	0.01066	0.2165	0.35	0.39	1.25. 10 <sup>-3</sup>	23.68	-6.78	-30.46		3.05. 10 <sup>-2</sup>	4.0. 10 <sup>3</sup>	
11.05		Tl <sub>2</sub> I <sub>3</sub> , TlI <sub>3</sub>	0.2844	3.3. 10 <sup>-4</sup>	0.2102	0.2805	0.1920	0.17	0.96. 10 <sup>-3</sup>	21.51	-6.59	-28.10		1.094	3.3. 10 <sup>3</sup>	
14.05		TlI <sub>3</sub> , I <sub>2</sub>	0.3588	1.36. 10 <sup>-3</sup>	0.1461	0.3090	0.1250	0.12	0.89. 10 <sup>-3</sup>	20.54	-6.97	-27.51		1.168	0.86. 10 <sup>3</sup>	
				(saturated.)												
6.10		Tl <sub>2</sub> I <sub>3</sub>	0.0951	2.98. 10 <sup>-5</sup>	0.0721	0.2155	0.72	0.71	1.17. 10 <sup>-3</sup>	23.71	-7.15	-30.86		0.987. 10 <sup>-1</sup>	3.3. 10 <sup>3</sup>	
8.10		"	0.1923	0.568. 10 <sup>-4</sup>	0.1476	0.2265	0.65	0.63	1.03. 10 <sup>-3</sup>	23.33	-7.04	-30.37		2.23. 10 <sup>-1</sup>	3.9. 10 <sup>3</sup>	
4.20		"	0.1955	2.44. 10 <sup>-5</sup>	0.1506	0.1939	1.51	1.37	0.98. 10 <sup>-3</sup>	24.44	-7.40	-32.84		0.981. 10 <sup>-1</sup>	4.0. 10 <sup>3</sup>	
7.20		"	0.2728	3.176. 10 <sup>-5</sup>	0.2136	0.1972	1.53	1.31	0.93. 10 <sup>-3</sup>	24.33	-7.37	-31.70		1.39. 10 <sup>-1</sup>	4.4. 10 <sup>3</sup>	

original concentration of potassium iodide, and (for greater accuracy) adding the concentration of free iodine, since the  $I_2$ -titre includes this.  $[I_3']$  was found by subtracting  $[I_2]$  (Column V.) together with the total concentration of thallium in the solution ( $= [TlI_4']$ : Column VI.) from the  $I_2$ -titre. The values of  $[I']$  and  $[I_3']$  thus found are really those of the total concentrations of the corresponding potassium salts, and should therefore be multiplied by the respective degrees of dissociation in order to yield the true concentrations of the ions; but since only the ratio enters into the formula, and the two salts are practically equally dissociated, no correction is necessary. Thus in terms of the values in the various columns, we have

$$k_j = \frac{V(II - IV + V)}{IV - V - VI}$$

The values of  $k_j$  found in this way are given in Column X., and show excellent agreement with one another, being more concordant than the values found by Jakowkin ( $0.77 - 1.44 \times 10^{-3}$ ), but of about the same mean value. Since this result depends upon the twofold application of the hypothesis that the ion  $TlI_4'$  is present, it constitutes a further confirmation of the correctness of this assumption.

Besides being a measure of the ratio  $\sqrt{[I_2]}/[I']$ , the oxydation potential simultaneously shows the ratio  $[Tl^{...}]/[Tl^.]$ , according to the relation

$$e = e_0 + 0.0295 \log \frac{[Tl^{...}]}{[Tl^.]}$$

Spencer and Abegg (*Zeit. anorg. Chem.*, **44**, 379 (1905)) showed that  $e_0$  in this formula has the value  $+0.916$  volt.

The values of  $\log_{10} \frac{[Tl^.]}{[Tl^{...}]}$  calculated from this expression are given in Column XI.

In all the solutions the  $Tl^{...}$  concentration is exceedingly small compared with the  $Tl^.$  concentration. Since no thalious thallium is analytically recognisable in the solution, while considerable quantities of thallic thallium are known to be

present, this gives us an insight into the stability of the thallic complex ion, which is, in fact, very great.

So far we have obtained only the ratio of the concentrations of the two thallium ions. The absolute concentrations can be readily calculated, however, for those solutions which are in equilibrium with solid thallous iodide (Nos. 1, 2 and 3). The solubility of thallous iodide was determined at 18° and 20·15° by Kohlrausch and Böttger respectively (Landolt and Börnstein, 3<sup>te</sup> Auf.). By extrapolation from their results Abegg and Maitland obtained the value  $2\cdot4 \times 10^{-4}$  gram mols. per litre at 25°, from which we have

$$L = [\text{TI}\cdot][\text{I}'] = 5\cdot8 \times 10^{-8}$$

whence 
$$[\text{TI}\cdot] = \frac{5\cdot8 \times 10^{-8}}{[\text{I}]}$$

Thus, using the values of  $[\text{I}']$  in Column VIII., we can calculate  $[\text{TI}\cdot]$  and  $[\text{TI}\cdots]$  for Nos. 1, 2 and 3. The values of  $\log_{10} [\text{TI}\cdot]$  and  $\log_{10} [\text{TI}\cdots]$  are shown in Columns XII. and XIII. respectively.

We can now calculate the stability constant of the ion  $\text{TIH}_4'$ , and in so doing we apply a rigorous test to the correctness of the formula. From the law of mass-action we have

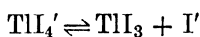
$$k_i = \frac{[\text{TIH}_4']}{[\text{TI}\cdots][\text{I}']^4}.$$

The concentration of the ion  $\text{TIH}_4'$  is given by the total thallium content of the solution (Column VI.), since no other compound of thallium and iodine possesses an analytically measurable solubility in water. Thus, using the values already found for  $[\text{TI}\cdots]$  (Column XIII.) and  $[\text{I}']$  (Column VIII.), the values of  $k_i$  are obtained for Nos. 1, 2, and 3. These are given in Column XIV.

$k_i$  must be constant also in those solutions which are not in equilibrium with solid thallous iodide, so that we can now calculate the  $\text{TI}\cdots$  concentration in these solutions, since  $[\text{TIH}_4']$  and  $[\text{I}']$  are known: and we thus also obtain the values of  $[\text{TI}\cdot]$  for these solutions, using the ratio in Column

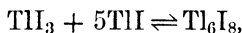
XI. The  $\text{TI}^{\cdots}$ - and  $\text{TI}^{\cdot}$ -concentrations thus found are given in Columns XII. and XIII.

Another relationship can be traced in the solutions which are not in equilibrium with  $\text{TII}$ . The complex ion  $\text{TII}_4'$  is in equilibrium with undissociated  $\text{TII}_3$  and  $\text{I}'$  according to the scheme



whence 
$$\frac{[\text{TII}_4']}{[\text{I}']} = k_n [\text{TII}_3]$$

The ratio  $[\text{TII}_4']/[\text{I}']$  is thus proportional to the concentration of undissociated  $\text{TII}_3$ . The values of  $k_n \times [\text{TII}_3]$ , obtained by dividing the total thallium concentration (Column VI.) by the  $\text{I}'$ -concentration (Column VIII.) are shown in Column XV. In accordance with the law of mass action, these values are constant for solutions in equilibrium with solid  $\text{TII}_3$ . Further, since



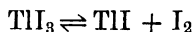
we obtain 
$$[\text{TII}_3] = \frac{[\text{TI}_6\text{I}_8]}{[\text{TII}]^5}$$

and the concentrations on the right-hand side of this equation become constant when the solution is in equilibrium with  $\text{TII}$  and  $\text{TI}_6\text{I}_8$  simultaneously. Hence  $k_n \times [\text{TII}_3]$  should also be constant in these solutions, and experiment shows that this is the case (Nos. 1, 2 and 3). A comparison of the values of  $k_n \times [\text{TII}_3]$  shows that in solutions in equilibrium with  $\text{TII}$  and  $\text{TI}_6\text{I}_8$  the concentration of  $\text{TII}_3$  is about

$$0.03 = \frac{2.9 \times 10^{-2}}{1.14} \text{ times}$$

that in solutions saturated with respect to  $\text{TII}_3$ .

Having thus obtained a measure of the concentration of undissociated  $\text{TII}_3$ , we may now attain a similar result for  $\text{TII}$ . Since



it follows that

$$[\text{TII}] = \text{const.} \times \frac{[\text{TII}_3]}{[\text{I}_2]}$$

so that by dividing the values in Column XV. by the corresponding concentrations of free iodine (Column V.) we obtain a series of values which are proportional to  $[TII]$ , (Column XVI.). These should be constant and maximal in solutions in equilibrium with solid  $TII$ . This is also actually the case (Nos. 1, 2 and 3). Numbers 4, 7 and 8 show values which are as high or a little higher, but the error is not large. Also these abnormal values occur in solutions which are rather concentrated with respect to potassium iodide.

Comparing these values, we find that the value of the  $TII$ -concentrations is always a very appreciable fraction of its saturation concentration. The lowest concentration, namely, that in saturated iodine solution, is about 0.22 ( $= \frac{0.86}{3.83}$ ) of the saturation value. Thus  $TII_3$ , even in equilibrium with solid iodine, acts as  $\frac{1}{5}$ th saturated  $TII$ , which agrees with the view of Wells and Penfield (*loc. cit.*) as to its constitution. This may be further tested by calculating the solubility product  $[Tl^+][I_3^-]$ . By means of the equation

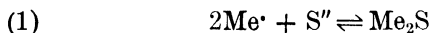
$$k_3 = \frac{[I_2][I']}{[I_3^-]}$$

we can calculate the value of  $[I_3^-]$  from the data in Columns V., VIII. and X. The values of the solubility product in the solutions saturated with  $TII_3$  are given in Column XVII., and show very satisfactory concordance, thus forming additional evidence for the view that  $TII_3$  exists for the most part in the form of thallous triiodide. The tautomeric character of the substance is clearly shown, however, by the fact that it readily yields the complex thallic ion  $TII_4'$ .

### B. The precipitation of sulphides.

The precipitation of metallic sulphides by hydrogen sulphide has a special interest on account of the great importance of the subject in analysis. While the analytical procedure has been built up empirically upon experience of its results, it is highly desirable to give the processes a theoretical groundwork.

In precipitating the sulphide of a mono-, di- or tri-valent metal respectively, the reactions are represented by the following equations:—



$$\text{whence} \quad \frac{[\text{Me}\cdot]^2[\text{S}'']}{[\text{Me}_2\text{S}]} = k_1$$

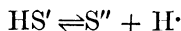


$$\text{whence} \quad \frac{[\text{Me}\cdot\cdot][\text{S}'']}{[\text{MeS}]} = k_2$$



$$\text{whence} \quad \frac{[\text{Me}\cdot\cdot\cdot]^2[\text{S}'']^3}{[\text{Me}_2\text{S}_3]} = k_3$$

The concentration of the sulphur ions is connected with the concentration of hydrogen sulphide as follows. Hydrogen sulphide dissociates in two stages according to the equations



$$\text{whence} \quad \frac{[\text{HS}'][\text{H}\cdot]}{[\text{H}_2\text{S}]} = k_1'$$

$$\text{and,} \quad \frac{[\text{H}\cdot][\text{S}'']}{[\text{HS}']} = k_2'$$

$$\text{or} \quad \frac{[\text{H}\cdot]^2[\text{S}'']}{[\text{H}_2\text{S}]} = k_1'k_2'$$

$$\text{Thus} \quad [\text{S}''] = k_1'k_2' \cdot \frac{[\text{H}_2\text{S}]}{[\text{H}\cdot]^2} = k' \frac{[\text{H}_2\text{S}]}{[\text{H}\cdot]^2}$$

Substituting, we obtain

$$\frac{[\text{Me}\cdot]^2[\text{H}_2\text{S}]}{[\text{H}\cdot]^2} = K_1$$

$$\frac{[\text{Me}\cdot\cdot][\text{H}_2\text{S}]}{[\text{H}\cdot]^2} = K_2$$

$$\frac{[\text{Me}\cdot\cdot\cdot]^2[\text{H}_2\text{S}]^3}{[\text{H}\cdot]^6} = K_3$$

and the corresponding solubility products are

$$L_1 = [\text{Me}']^2[\text{S}''] = k'K_1$$

$$L_2 = [\text{Me}''][\text{S}'''] = k'K_2$$

$$L_3 = [\text{Me}''']^2[\text{S}''']^3 = k'^3K_3$$

$k_1'$ , the first dissociation constant of hydrogen sulphide, was determined by Auerbach (*Zeit. phys. Chem.*, **49**, 217 (1904)) from measurements of the conductivity of its aqueous solution. The first dissociation only was taken into account, since the second dissociation constant of a weak dibasic acid is always minute compared with the first one. In this way Auerbach found a series of values of  $k_1'$  for solutions of various concentrations of hydrogen sulphide which showed excellent agreement amongst themselves, and gave the mean value  $0.91 \times 10^{-7}$  at  $18^\circ$ .

$k_2'$ , the second dissociation constant, has also been measured (Knox, *Trans. Farad. Soc.*, Vol. IV. Part I. (1908)) by a method which will be discussed later. Its value is  $1.2 \times 10^{-15}$  at  $25^\circ$ . Hence  $k_1' \cdot k_2' = k' = 0.91 \times 10^{-7} \times 1.2 \times 10^{-15} = 1.09 \times 10^{-22}$  at  $25^\circ$  very nearly, and

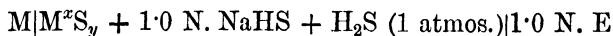
$$L_1 = 1.09 \times 10^{-22} \cdot K_1$$

$$L_2 = 1.09 \times 10^{-22} \cdot K_2$$

$$L_3 = 1.30 \times 10^{-60} \cdot K_3$$

Thus, if we know  $L$  we can calculate  $K$ , and *vice versâ*. These constants have been measured for nearly all the heavy metals.

Bernfeld (*Zeit. phys. Chem.*, **25**, 46 (1898)) measured the potentials of cells of the type



using the metals silver, lead and bismuth. From the experimentally determined E.M.F.'s the concentrations of the metal ions were calculated, using the known values of their respective electrolytic potentials. Bernfeld found the concentrations of the metal ions in a 1.0 N. sodium hydro-

sulphide saturated with hydrogen sulphide at a pressure of one atmosphere and with the metallic sulphide to be

$$[\text{Ag}\cdot] = 3.4 \times 10^{-22}$$

$$[\text{Pb}\cdot\cdot] = 1.45 \times 10^{-5}$$

$$[\text{Bi}\cdot\cdot\cdot] = 0.7 \times 10^{-26}$$

It has since been shown, however, that the value for lead is incorrect. This will be discussed later.

Lucas (*Zeit. anorg. Chem.*, **41**, 193 (1904)) measured the solubility of silver sulphide in potassium cyanide, and using the known value of the constant

$$K = \frac{[\text{Ag}\cdot][\text{CN}' ]^3}{[\text{Ag}(\text{CN})_3'']}$$

(Bodländer and Eberlein, *loc. cit.*), was able to calculate the concentration of the silver ions. His calculation of the concentration of the sulphur ions is, however, incorrect.<sup>1</sup>

Glixelli (*Zeit. anorg. Chem.*, **55**, 297 (1907)) studied analytically the precipitation of zinc sulphide in acid and in alkaline solutions, and showed that in acid solution the precipitation leads to a false equilibrium, the reaction coming to a stop at a point which cannot be approached from both sides. In alkaline solution  $K_2 = 5 \times 10^{-5}$ .

A very thorough study of the behaviour of the sulphur anion was made by Knox (*Trans. Farad. Soc.*, Vol. IV. Part I. (1908)), who determined, amongst other things, the

<sup>1</sup> Lucas points out that in calculating the concentration  $[\text{S}'' ]$  we must allow for the hydrolysis of both the potassium sulphide and the potassium cyanide. He gives the equation

$$\frac{[\text{H}\cdot][\text{OH}']}{[\text{CN}']} = 1.2 \times 10^{-5}$$

which is obviously incorrect. For  $[\text{H}\cdot]$  we should read  $[\text{HCN}]$ . In this case, however, we could only solve for  $[\text{OH}']$  by putting  $[\text{OH}'] = [\text{HCN}]$ . This would be allowable in a solution containing potassium cyanide alone, and might be so in the mixed solution, seeing that the solubility of silver sulphide in potassium cyanide solutions is small. Recalculation from Lucas's experimental results, however, showed that this had not been done. Lucas does not give the method by which his calculations were made.



value of the second dissociation constant of hydrogen sulphide. This, in conjunction with the value of the first constant found by Auerbach (*loc. cit.*) enables us to calculate K and L for the various sulphides, the concentrations of whose metal ions in solutions of sodium hydrosulphide have been determined by other observers.

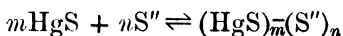
Knox began by studying the reaction in virtue of which mercuric sulphide is dissolved to a considerable extent by solutions of sodium sulphide. In the light of the formula established by Knox, this reaction may be regarded as leading to the formation either of the complex salt  $\text{HgSSNa}_2$ , yielding the complex anion  $\text{HgSS}''$ , or of the salt  $\text{Na—S—Hg—S—Na}$ , in which only the usually-accepted valencies are exercised.

The following table shows the values of the solubility of red and black mercuric sulphide in sodium sulphide solutions at  $25^\circ$  :—

Conc. $\text{Na}_2\text{S}$ Mol./litre.	HgS (red) dissolved Mol./litre.	Ratio HgS (red) : $\text{Na}_2\text{S}$ .	HgS(black) dissolved Mol./litre.	Ratio HgS (black) HgS (red)
2.030	1.144	0.5635	—	—
1.52	0.7832	0.5153	0.8561	1.09
1.015	0.4423	0.4328	0.5002	1.13
0.755	0.2878	0.3812	0.3336	1.16
0.50	0.1500	0.3006	0.1805	1.20
0.25	0.04544	0.1818	0.05622	1.24
0.10	0.008241	0.0824	0.01085	1.32

The fact that black mercuric sulphide is more soluble than the red variety (the solution in each case having the same constitution) proves that the black form is the unstable one. This is supported by the following circumstances : (1) when hydrogen sulphide is passed into the above solutions, black mercuric sulphide is precipitated. (2) The black sulphide is slowly converted into the red form on standing in contact with the solution.

The complex formation may, as usual, be represented by the scheme



Applying the law of mass-action, we obtain

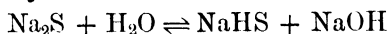
$$\frac{[\text{HgS}]^m[\text{S}'']^n}{[(\text{HgS})_m(\text{S}'')_n]} = K$$

or

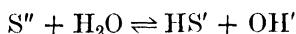
$$[(\text{HgS})_m(\text{S}'')_n] = K[\text{HgS}]^m[\text{S}'']^n$$

In saturated solution  $[\text{HgS}]^m$  is constant, so that the solubility (which is practically the concentration of the complex ion) is proportional to  $[\text{S}'']^n$ .

Now, sodium sulphide hydrolyses according to the equation



or, leaving out the sodium ions, whose concentration remains practically unchanged,



Hence

$$\frac{[\text{HS}'][\text{OH}']}{[\text{S}'']} = k_h$$

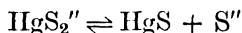
$k_h$  being the hydrolysis constant of sodium sulphide. From this equation we can see that by increasing the concentration of hydroxyl ions we shall diminish the degree of hydrolysis of the sodium sulphide, thus causing  $[\text{HS}']$  to grow smaller and  $[\text{S}'']$  to increase by the same amount; and since the solubility of mercuric sulphide in the solution is proportional to  $[\text{S}'']^n$ , addition of caustic soda should increase this. The following table shows the solubility of red mercuric sulphide in various solutions of sodium sulphide and caustic soda:—

Conc. $\text{Na}_2\text{S}$ Mol./litre	HgS (red) dissolved in Mols./litre						Ratio HgS : $\text{Na}_2\text{S}$ in solutions with 7.7 N. NaOH.
	In pure $\text{Na}_2\text{S}$ .	With 0.5 N. NaOH.	With 1.0 N. NaOH.	With 4.48 N. NaOH.	With 4.67 N. NaOH.	With 7.7 N. NaOH.	
1.015	0.4423	—	0.673	—	—	0.9167	0.903
0.755	0.2878	—	0.485	—	—	—	—
0.50	0.1500	0.2483	0.302	0.435	—	0.4637	0.927
0.25	0.04544	0.1106	0.148	—	0.225	0.2369	0.948
0.10	0.008241	0.03962	0.0563	—	0.0903	0.09634	0.963

In the strongly alkaline solutions the concentration of HgS becomes nearly equal to that of  $\text{Na}_2\text{S}$ , so that if each HgS molecule takes up one sulphur ion, only a small quantity of sulphur ions can remain and the degree of hydrolysis must be small. Thus, unless  $m$  is greater than one, the formula of the complex salt must be  $\text{Na}_2\text{HgS}_2$  and that of the complex anion  $\text{HgS}_2''$ .

This conclusion was supported by the results of potential measurements. Owing to the difficulty of determining exactly the concentration of  $\text{S}''$  ions, the application of this method was at first limited to the measurement of the E.M.F.'s of cells containing equal quantities of sodium sulphide and small but different amounts of HgS, thus allowing only of the calculation of  $m$ . In this way it was found that  $m = 1$ , so that the formula for the complex ion must be  $\text{HgS}_2''$ , and  $n = 1$  also. Assuming this formula, the potential method was now applied as follows:—

The complex ion must dissociate into its single ion and neutral part according to the equation



so that in solutions saturated with respect to HgS,

$$[\text{HgS}_2''] = K[\text{HgS}][\text{S}''] = k_x[\text{S}'']$$

since the concentration of HgS is constant.

For the dissociation of HgS the mass-action equation is

$$[\text{HgS}] = k_4[\text{Hg}^{..}][\text{S}'']$$

and since HgS is constant, this gives

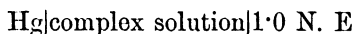
$$[\text{S}''] = \frac{k_5}{[\text{Hg}^{..}]}$$

Substituting in the first equation, we get

$$[\text{HgS}_2''] = \frac{k_x k_5}{[\text{Hg}^{..}]} = \frac{k_6}{[\text{Hg}^{..}]}$$

Hence, if  $m = n = 1$ , the product  $[\text{HgS}_2''][\text{Hg}^{..}]$  is constant in all saturated solutions.  $[\text{HgS}_2'']$  is practically equal to the

concentration of dissolved  $\text{HgS}$ , and  $[\text{Hg}^{''}]$  can be found by measuring the potential of the cell



The concentration of mercuric ions in the normal electrode was found by Ley and Heimbucher (*loc. cit.*) to be  $3 \times 10^{-20}$  gram ions per litre.

Hence, if  $e$  be the E.M.F. of the cell (the normal electrode being positive)

$$e = 0.0295 \log \frac{3 \times 10^{-20}}{[\text{Hg}^{''}]}$$

The following table shows the results obtained in this way :—

Conc. $\text{Na}_2\text{S}$ Mol./litre.	Conc. $\text{HgS}_2^{''}$ = dissolved $\text{HgS}$ Mol./l.	E.M.F. against 1.0 N. E.	$[\text{Hg}^{''}]$ .	$[\text{Hg}^{''}][\text{HgS}_2^{''}] = k_6$
2.030	1.144	- 0.9715	$3.53 \times 10^{-53}$	$4.0 \times 10^{-53}$
1.52	0.7832	- 0.9650	$5.21 \times 10^{-53}$	$4.1 \times 10^{-53}$
1.015	0.4423	- 0.9570	$10.9 \times 10^{-53}$	$4.8 \times 10^{-53}$
0.755	0.2878	- 0.9515	$16.5 \times 10^{-53}$	$4.7 \times 10^{-53}$
0.50	0.1500	- 0.9455	$26.7 \times 10^{-53}$	$4.0 \times 10^{-53}$
0.25	0.04544	- 0.9335	$58.5 \times 10^{-53}$	$2.7 \times 10^{-53}$
0.10	0.008241	- 0.9145	$300 \times 10^{-53}$	$2.5 \times 10^{-53}$

No attempt was made to allow for diffusion potentials. Knox states that the E.M.F.'s were reproducible to within a millivolt.

The concentrations of mercury ions in these solutions are so small that the ordinary conception of a potential between a solution and an electrode in terms of the kinetic theory of gases and solutions breaks down entirely. If we take the number of molecules in a gram molecule as being, in round numbers,  $10^{24}$ , we see that a solution containing  $10^{-53}$  gram ions of mercury per litre is equivalent to  $10^{29}$  litres of water containing one single mercury ion! The electrochemical reaction must therefore be looked upon as produced by the other ions present which are potentially in equilibrium with

mercury ions at this concentration. The point had already been discussed by Haber, Bodländer, Abegg and Daneel (*Zeit. für Elektrochemie*, **10**, 403, 604, 607, 609, and 773 (1904)). (See Le Blanc, *Lehrbuch der Elektrochemie*, 4<sup>te</sup> Auf., p. 189.)

From the equation

$$[\text{OH}'][\text{HS}'] = k_h[\text{S}']$$

we obtain for solutions containing no added  $\text{H}_2\text{S}$  or  $\text{NaOH}$

$$[\text{HS}']^2 = k_h[\text{S}']$$

since

$$[\text{OH}'] = [\text{SH}']$$

Further, assuming complete electrolytic dissociation of  $\text{NaHS}$  and  $\text{Na}_2\text{S}$ , we have

$$[\text{HS}'] + [\text{S}'] = a - b$$

where  $a$  is the total initial concentration of  $\text{Na}_2\text{S}$  and  $b$  that of the dissolved  $\text{HgS}$ , *i.e.* that of the complex salt. From these two equations we get

$$[\text{HS}'] = -\frac{k_h}{2} + \sqrt{\frac{k_h^2}{4} + k_h(a - b)}$$

and

$$[\text{S}'] = a - b - [\text{HS}']$$

Thus if we assume a value for  $k_h$ , we can find  $[\text{S}']$ , in the solutions used in the above measurements, and thus also  $L$ , the solubility product of mercuric sulphide, and  $k_s$ , the stability constant of the complex ion, which is given by the equation

$$k_s = \frac{[\text{HgS}_2'']}{[\text{Hg}][\text{S}'']^2}$$

From Küster's measurements (*Zeit. phys. Chem.*, **30**, 128 (1900)) Knox calculated  $k_h = 0.274$ . This value gave very unsatisfactory results, however, when inserted in the above expressions, and as the solubility and potential measurements show that a definite complex ion,  $\text{HgS}_2''$ , predominates strongly in these solutions and dissociates according to the law of mass-action, a value of  $k_h$  was found by trial which

# SOME SPECIAL CASES OF EQUILIBRIUM 127

gave satisfactory results. The following table shows the results of Knox's calculations:—

Conc. $\text{Na}_2\text{S}$ Mol./litre.	Conc. $\text{S}''$ gram. ion/l.	$\frac{[\text{Hg}^{++}][\text{S}'']}{L}$	$\frac{[\text{HgS}_2'']}{[\text{Hg}^{++}][\text{S}'']^2} = k_s.$
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$k_h = 0.405$ . This gives hydrolysis in 0.05 M. solution = 90 per cent.

2.03	0.456	$1.6 \times 10^{-53}$	$1.6 \times 10^{53}$
1.52	0.356	$1.8 \times 10^{-53}$	$1.2 \times 10^{53}$
1.015	0.252	$2.7 \times 10^{-53}$	$0.64 \times 10^{53}$
0.755	0.189	$3.1 \times 10^{-53}$	$0.49 \times 10^{53}$
0.50	0.125	$3.3 \times 10^{-53}$	$0.36 \times 10^{53}$
0.25	0.0549	$3.2 \times 10^{-53}$	$0.25 \times 10^{53}$
0.10	0.0145	$4.4 \times 10^{-53}$	$0.13 \times 10^{53}$

$k_h = 1.0$ . This gives hydrolysis in 0.05 M. solution = 95 per cent.

2.03	0.320	$1.1 \times 10^{-53}$	$3.2 \times 10^{53}$
1.52	0.243	$1.3 \times 10^{-53}$	$2.4 \times 10^{53}$
1.015	0.166	$1.8 \times 10^{-53}$	$1.5 \times 10^{53}$
0.755	0.120	$2.0 \times 10^{-53}$	$1.2 \times 10^{53}$
0.50	0.075	$2.0 \times 10^{-53}$	$0.99 \times 10^{53}$
0.25	0.0402	$2.4 \times 10^{-53}$	$0.48 \times 10^{53}$
0.10	0.0072	$2.2 \times 10^{-53}$	$0.53 \times 10^{53}$

$k_h = 5$ . This gives hydrolysis in 0.05 M. solution = 99 per cent.

2.03	0.118	$0.42 \times 10^{-53}$	$23 \times 10^{53}$
1.52	0.0848	$0.44 \times 10^{-53}$	$21 \times 10^{53}$
1.015	0.0537	$0.58 \times 10^{-53}$	$14 \times 10^{53}$
0.755	0.0372	$0.61 \times 10^{-53}$	$13 \times 10^{53}$
0.50	0.0217	$0.58 \times 10^{-53}$	$12 \times 10^{53}$
0.25	0.0076	$0.44 \times 10^{-53}$	$13 \times 10^{53}$
0.10	0.00176	$0.53 \times 10^{-53}$	$9 \times 10^{53}$

$k_h = 10$ . This gives hydrolysis in 0.05 M. solution = 99.5 per cent.

2.03	0.067	$0.24 \times 10^{-53}$	$7.2 \times 10^{53}$
1.52	0.048	$0.25 \times 10^{-53}$	$6.5 \times 10^{53}$
1.105	0.030	$0.33 \times 10^{-53}$	$4.5 \times 10^{53}$
0.755	0.022	$0.36 \times 10^{-53}$	$3.6 \times 10^{53}$
0.50	0.011	$0.29 \times 10^{-53}$	$4.6 \times 10^{53}$
0.25	0.0041	$0.24 \times 10^{-53}$	$4.6 \times 10^{53}$
0.10	0.00076	$0.23 \times 10^{-53}$	$4.8 \times 10^{53}$

We may therefore take as a probable value

$$k_h = 10$$

In order to throw further light upon this result measurements were made of the speed of decomposition of diacetone alcohol in presence of caustic soda and sodium sulphide respectively. The reaction mixture was placed in a dilatometer, and the change in volume noted as the reaction proceeded. In this way it was shown that 0.1 M. and 0.05 M. solutions of sodium sulphide are nearly completely hydrolysed. The method is insufficiently accurate to give the degree of hydrolysis to within one or two per cent., but it is certainly greater than 95 per cent., and thus much higher than the value given by Küster.

It is interesting to notice that Knox prepared a solid double sulphide of sodium and mercury which has the composition represented by the formula  $2\text{Na}_2\text{S}$ ,  $5\text{HgS}$ ,  $3\text{H}_2\text{O}$ . This is a further case where the solid which separates from a solution has a different composition from the predominating component in the liquid (Chapter VIII), and indicates that probably other less stable complex ions are present to some extent in the solution.

Having found the value of  $k_h$  we can now calculate the second dissociation constant of hydrogen sulphide, namely

$$k_2' = \frac{[\text{H}\cdot][\text{S}'']{}}{[\text{HS}]}$$

From the equations

$$[\text{H}\cdot][\text{OH}'] = k_w = 1.2 \times 10^{-14}$$

and

$$[\text{HS}'][\text{OH}'] = k_h[\text{S}''']$$

we obtain

$$\frac{[\text{H}\cdot][\text{S}''']{}}{[\text{HS}]} = k_2' = \frac{k_w}{k_h}$$

Since

$$k_w = 1.2 \times 10^{-14} \text{ and } k_h = 10$$

we have

$$k_2' = \frac{1.2 \times 10^{-14}}{10} = 1.2 \times 10^{-15}$$

This result is of the utmost importance, as it enables us to

calculate the ratio  $\frac{[S'']}{[HS']}$  in any solution in which we know the value of  $[H\cdot]$  or  $[OH']$ . A few examples, taken from Knox's paper, will make this clear.

We have the relationship

$$\frac{[S'']}{[HS']} = \frac{k_2'}{[H\cdot]} = \frac{1.2 \times 10^{-15}}{[H\cdot]} = 0.1[OH']$$

In *neutral* solution ( $[OH'] = 1.1 \times 10^{-7}$ )

$$[S''] = 1.1 \times 10^{-8}[HS']$$

In 1.0 N. acid solution ( $[OH'] = 1.2 \times 10^{-14}$ )

$$[S''] = 1.2 \times 10^{-15}[HS']$$

In 1.0 N. basic solution ( $[OH'] = 1.0$ )

$$[S''] = 0.1[HS']$$

and in 10 N. basic solution ( $[OH'] = 10$ )

$$[S''] = [HS']$$

The saturation concentration of hydrogen sulphide in aqueous solution is very nearly 0.1 molar. From Auerbach's measurements we have

$$k_1' = \frac{[HS'][H\cdot]}{[H_2S]} = 9.1 \times 10^{-8}$$

In this solution

$$[HS'] = [H\cdot]$$

and therefore

$$[H\cdot] = [HS'] = \sqrt{0.1 \times 9.1 \times 10^{-8}} = 0.95 \times 10^{-4}$$

Further, since

$$k_2' = \frac{[H\cdot][S'']}{[HS']} = 1.2 \times 10^{-15}$$

we have  $[S''] = 1.2 \times 10^{-15}$

Again in 1.0 M.  $Na_2S$  solution

$$k_h = \frac{[HS'][OH']}{[S'']} = 10,$$

$$[HS'] = [OH']$$

and  $[S''] + [HS'] = 1.0$



assuming complete electrolytic dissociation. These equations give

$$[\text{HS}'] = [\text{OH}'] = 0.91$$

and

$$[\text{S}''] = 0.09$$

Finally, in a solution of NaHS we have

$$k_1' = \frac{[\text{HS}'][\text{H}^+]}{[\text{H}_2\text{S}]} = 9.1 \times 10^{-8}$$

and

$$k_w = [\text{H}^+][\text{OH}'] = 1.2 \times 10^{-14}$$

Hence the hydrolysis constant,  $\frac{k_w}{k_1'}$ , is

$$\frac{k_w}{k_1'} = \frac{[\text{H}_2\text{S}][\text{OH}']}{[\text{HS}]} = \frac{1.2 \times 10^{-14}}{9.1 \times 10^{-8}} = 1.3 \times 10^{-7}$$

In a 1.0 M. solution, we have

$$[\text{H}_2\text{S}] = [\text{OH}']$$

and

$$[\text{HS}'] = 1, \text{ very nearly}$$

$$\text{Hence } [\text{H}_2\text{S}] = [\text{OH}'] = \sqrt{1.3 \times 10^{-7}} = 3.6 \times 10^{-4}$$

$$\text{Now } [\text{H}^+] = \frac{k_w}{[\text{OH}']} = \frac{1.2 \times 10^{-14}}{3.6 \times 10^{-4}} = 3.3 \times 10^{-11}$$

$$\text{Hence } [\text{S}''] = \frac{k_2'[\text{HS}']}{[\text{H}^+]} = \frac{1.2 \times 10^{-15} \times 1}{3.3 \times 10^{-11}} = 3.6 \times 10^{-5}$$

On account of the great importance of these results we may reproduce the following table (Knox), including the foregoing and some others:—

Solution.	[S'']	[HS']	[H <sub>2</sub> S]	[H <sup>+</sup> ]	[OH']
1.0 M. Na <sub>2</sub> S	0.09	0.91	$1.3 \times 10^{-7}$	$1.3 \times 10^{-14}$	0.91
1.0 M. NaHS	$3.6 \times 10^{-5}$	1	$3.6 \times 10^{-4}$	$3.3 \times 10^{-11}$	$3.6 \times 10^{-4}$
1.0 M. (NH <sub>4</sub> ) <sub>2</sub> S	$2.4 \times 10^{-6}$	ca. 1	$5.5 \times 10^{-3}$	$5 \times 10^{-10}$	$2.3 \times 10^{-5}$
1.0 M. NH <sub>4</sub> HS	$1.6 \times 10^{-7}$	0.93	0.07	$0.7 \times 10^{-8}$	$1.7 \times 10^{-6}$
Sat. aqueous H <sub>2</sub> S	$1.2 \times 10^{-15}$	$0.95 \times 10^{-4}$	0.1	$0.95 \times 10^{-4}$	$1.3 \times 10^{-10}$
Sat. H <sub>2</sub> S + 1.0 N. acetic acid	$0.65 \times 10^{-18}$	$2.1 \times 10^{-6}$	0.1	$4.2 \times 10^{-3}$	$3 \times 10^{-12}$
Sat. H <sub>2</sub> S + 1.0 N. HCl	$1.1 \times 10^{-23}$	$0.91 \times 10^{-8}$	0.1	1.0	$1.2 \times 10^{-14}$

Knox also made measurements of the E.M.F.'s of cells of the type



where M was an electrode of silver, lead or copper respectively, and found that the concentrations of the metal ions in 0.1 M.  $\text{Na}_2\text{S}$  were

$$[\text{Ag}^+] = 6.3 \times 10^{-24}$$

$$[\text{Pb}^{++}] = 2.6 \times 10^{-12}$$

$$[\text{Cu}^{++}] = 1.2 \times 10^{-39}$$

A 0.1 M. solution of  $\text{Na}_2\text{S}$  is 0.001 M. with respect to  $\text{S}''$  ions, and we thus obtain the solubility products

$$[\text{Ag}^+]^2[\text{S}''] = 3.9 \times 10^{-50}$$

$$[\text{Pb}^{++}][\text{S}''] = 2.6 \times 10^{-15}$$

$$[\text{Cu}^{++}][\text{S}''] = 1.2 \times 10^{-42}$$

As was remarked in the case of Bernfeld's measurements, the value of the solubility product for lead sulphide found in this way is incorrect. From the results for silver and copper we obtain the solubility values  $2.2 \times 10^{-17}$  and  $1.1 \times 10^{-21}$  respectively.

From the concentration of mercury ions in sodium sulphide solutions saturated with mercuric sulphide we obtain

$$[\text{Hg}^{++}][\text{S}'''] = L_{\text{HgS}} = 2.8 \times 10^{-54}$$

whence the solubility of mercuric sulphide in water is  $1.7 \times 10^{-27}$  gram mol. per litre.

Bruner and Zawadski (*Zeit. anorg. Chem.*, **65**, 136 (1909); correction, *ibid.*, **67**, 454 (1910)) studied several further cases of sulphide precipitation analytically, thus avoiding the errors incidental to potential measurements. The sulphides studied in this way were those of thallium, iron, cadmium and lead.

As the mean of many determinations of the equilibrium point, approached from both sides, *i.e.* both by partial solution

of the sulphide in acid, and by precipitation with hydrogen sulphide, the value

$$K_1 = \frac{[\text{Tl}^+]^2[\text{H}_2\text{S}]}{[\text{H}^+]^2} = 0.637$$

was obtained. Remembering that

$$L_1 = 1.092 \times 10^{-22} K_1$$

this gives us

$$L_1 = 7.0 \times 10^{-23}$$

Experiments were also made on the precipitation of thallium sulphide in presence of other sulphides. The results showed that the equilibrium is affected by the sulphides of arsenic, antimony, tin, mercury and copper. The values of  $K_1$  were plotted against the molecular composition of the precipitate, and in this way it was shown that thallium sulphide forms two compounds with copper sulphide corresponding to the formulæ  $\text{Tl}_2\text{S}_4\text{CuS}$  and  $\text{Tl}_2\text{S}_2\text{CuS}$  respectively. From the fact that the curve dips between these two points, Bruner and Zawadski consider that these two compounds form a solid solution. When the amount of  $\text{Tl}_2\text{S}$  in the precipitate exceeds 36 per cent. the constant again becomes 0.637, indicating that the thallium sulphide is present as a separate phase.

With arsenic sulphide, thallium sulphide forms a continuous series of solid solutions from pure  $\text{As}_2\text{S}_3$  to a solution containing 73.5 per cent. of  $\text{Tl}_2\text{S}$  molecules. When more thallium sulphide than this is present it appears as a separate phase. (For the recognition of other solid solutions by the study of equilibria in solution, see Abegg and Scholtz (*Zeit. für Elektrochemie*, **12** (1906)).)

Analytical determinations of the equilibrium point in the case of iron gave

$$\begin{aligned} K_2 &= 3.4 \times 10^9 \\ L_2 &= 3.7 \times 10^{-19} \end{aligned}$$

In the case of cadmium the results depended to some extent upon the method of precipitation of the sulphide.

Thus, for the precipitation of cadmium sulphide from the sulphate solution,

$$K_2 = 4.6 \times 10^{-7}$$

while for the product from the chloride,

$$K_2 = 6.6 \times 10^{-6}$$

This can only be interpreted by assuming that cadmium sulphide can exist in two or more modifications.

The analytical results obtained for lead showed

$$K_2 = 3.1 \times 10^{-6}$$

$$L_2 = 3.4 \times 10^{-28}$$

in startling contrast with the values obtained by Bernfeld (*loc. cit.*) and Knox (*loc. cit.*) from potential measurements. Knox's measurements gave for lead

$$L_2 = 2.6 \times 10^{-15}$$

Thus the potentials measured by Bernfeld and Knox appear to correspond to a concentration of lead ions about  $10^{13}$  times too great, or, in other words, the E.M.F. of the lead electrode is about  $13 \times 0.0295 = \text{ca. } 0.4$  volt too high.

Further light has recently been thrown on this point by Lebedew (*Zeit. Elektrochemie*, **18**, 891 (1912)). Lebedew repeated the potential measurements and obtained constant and reproducible values which agreed well with Bernfeld's. It therefore became necessary to consider possible errors in the theory for the cells measured. Experiments were therefore made in order to ascertain whether the lead-lead sulphide electrode is really reversible. On substituting a platinum plate for the lead electrode in a sodium hydrosulphide solution it was found that a definite E.M.F. was produced which was almost exactly equal to that of a lead electrode dipping into the same liquid. Thus it is evident that (1) lead becomes passive in sodium hydrosulphide solution, (2) that some other electrochemical reaction occurs at a lead or other indifferent electrode in sodium hydrosulphide solution which produces a definite E.M.F. The nature of this reaction is unknown.

If we know the solubility product of the sulphide of a metal whose electrolytic potential we also know, we can obtain an approximate value for the electrolytic potential of sulphur.

In a reversible cell of the type

Metal|saturated metallic sulphide|Sulphur

if we pass a current from left to right the sulphide is formed, while by passing the current from right to left we decompose the sulphide into its elements. Since the solution is in equilibrium with the solid sulphide, the free energy of the reaction is the free energy of formation or decomposition of the solid sulphide, and it is measured by  $nFE$ ,  $E$  being the decomposition potential. We may split this E.M.F. into two parts, being the E.M.F.'s of the electrodes

Metal|Saturated metallic sulphide

and Sulphur|Saturated metallic sulphide.

In order that  $nFE$  shall represent the positive energy which we require to expend on the system to decompose one gram molecule of the sulphide, we must reckon the E.M.F. of the metal electrode positive when the electrode is negative to the solution, and the E.M.F. of the sulphur electrode positive when the electrode is positive to the solution. The values taken in this way when the solutions contain one gram ion per litre are the thermodynamic electrode potentials, and are expressed numerically using either the hydrogen electrode or the normal calomel electrode as nullpoint.<sup>1</sup>

Calling  $E_s$ ,  $E_A$ , and  $E_K$  the decomposition potential and the electrolytic potentials of the anion and kation respectively, we obtain the relation

$$E_s = E_A + E_K + \frac{RT}{n_a F} \log \frac{1}{c_a} + \frac{RT}{n_k F} \log \frac{1}{c_k}$$

<sup>1</sup> Another mode of expressing these values is also in use, in which the signs of the potentials are reversed. This has been used in the preceding chapters. In the system used in this section, the electrolytic potential represents the relative tendency of the metal or non-metal to go into solution, while in the other system, which was used in the previous chapters, the electrolytic potential represents the tendency of the metal or non-metal to come out of solution.

where  $c_a$  and  $c_k$  are the concentrations of the anions and kations in gram ions per litre, and  $n_a$  and  $n_k$  are their valencies. If  $A$  and  $Q$  be the free energy of formation and the heat of formation respectively of the solid sulphide, we have

$$A = Q + T \frac{dA}{dT}$$

If  $T \frac{dA}{dT}$  be small compared with  $Q$ , we may write

$$A = Q$$

Hence 
$$E_s = \frac{A}{nF} = \frac{Q}{nF}$$

if  $Q$  be expressed in joules, and  $n$  be the number of faradays required for the electrolytic decomposition of one gram molecule of the sulphide; or, expressing  $Q$  in calories,

$$E_s = \frac{4.189Q}{n \times 96540} = \frac{Q}{n \times 23046}$$

Therefore

$$\frac{Q}{n \times 23046} = E_A + E_K + \frac{RT}{n_a F} \log \frac{1}{c_a} + \frac{RT}{n_k F} \log \frac{1}{c_k}$$

This gives for monovalent metals

$$\begin{aligned} \frac{Q}{2 \times 23046} &= E_A + E_K + \frac{RT}{2F} \log \frac{1}{c_a} + \frac{RT}{F} \log \frac{1}{c_k} \\ &= E_A + E_K + \frac{RT}{2F} \log \frac{1}{c_a} + \frac{RT}{2F} \log \frac{1}{c_k^2} \\ &= E_A + E_K - \frac{RT}{2F} \log (c_a \cdot c_k^2) \\ &= E_A + E_K - \frac{RT}{2F} \log L_1 \end{aligned}$$

Similarly, for divalent metals

$$\begin{aligned} \frac{Q}{2 \times 23046} &= E_A + E_K - \frac{RT}{2F} \log (c_a \cdot c_k) \\ &= E_A + E_K - \frac{RT}{2F} \log L_2. \end{aligned}$$

and for the sulphides of the trivalent metals (formula  $M_2S_3$ )

$$\begin{aligned}\frac{Q}{6 \times 23046} &= E_A + E_K - \frac{RT}{2F} \log c_a - \frac{RT}{3F} \log c_k \\ &= E_A + E_K - \frac{RT}{6F} \log c_a^3 - \frac{RT}{6F} \log c_k^2 \\ &= E_A + E_K - \frac{RT}{6F} \log L_3\end{aligned}$$

Thus, in general,

$$\frac{Q}{n \times 23046} = E_A + E_K - \frac{RT}{nF} \log L$$

Now, Bodländer (*Zeit. phys. Chem.*, **27**, 55 (1898)) showed that this general equation, when solved for  $L$ , gave values for the solubilities of a large number of salts which agreed approximately with the values found by other means. We may therefore solve for  $E_A$  if the solubility of the salt be known. This is the single method which has as yet been found for measuring the electrolytic potential of sulphur.

Bruner and Zawadski, in the course of their determination of the equilibrium constant for thallium sulphide, measured its temperature coefficient. From this they calculate

$$L_1(18^\circ) = 4.5 \times 10^{-23}$$

At  $18^\circ$  the above formula becomes

$$\frac{Q}{2 \times 23046} = E_A + E_K - 0.029 \log_{10} L_1$$

Inserting the values of  $Q$  (19650 calories (Thomsen)),  $E_K$  (0.322 volt against the hydrogen electrode (Wilsmore, *Zeit. phys. Chem.*, **35**, 291 (1900))) and  $L$  ( $4.5 \times 10^{-23}$ ), we obtain

$$E_A = -0.543 \text{ volt}$$

against the hydrogen electrode.

Bruner and Zawadski took as the denominator on the left-hand side of the equation the value  $2 \times 23100$ , and thus found  $E_A = -0.545$  volt. The electrolytic potential of thallium had been redetermined a short time previously by

Brislee (*Trans. Faraday Soc.*, Dec., 1908), who found the value to be +0.3195 volt against the hydrogen electrode.

If we recalculate the electrolytic potential of sulphur from Bruner and Zawadski's results, using this value, we obtain

$$E_A = -0.5475 \text{ volt}$$

Taking the denominator on the left-hand side of the equation as 23046, however (the more exact value), we get

$$E_A = -0.5455 \text{ volt}$$

Thus the two small errors practically neutralise one another, and the value calculated by Bruner and Zawadski is almost unaffected.

From this value we can now calculate the solubility of any other sulphide of which we know the heat of formation. The following table (Bruner and Zawadski, *loc. cit.*) shows the values of  $L$  for a number of sulphides calculated from the experimental data of various observers relating to equilibria in solution on the one hand, and calculated from the heat of formation on the other, using the value

$$E_A = -0.545 \text{ volt}$$

The values of  $Q$  taken were those of Thomsen excepting where otherwise indicated.

Considering the inaccuracy introduced into the calculations by putting

$$A = Q$$

the agreement between the two sets of values is excellent. It may be noticed that the error grows more important as  $Q$  grows smaller (see, for example, Nernst, *Theoretische Chemie*, 5<sup>te</sup> Auf., pp. 727, 728), and correspondingly we find that the calculated values (from heat of formation) lie closest to the experimental ones (from equilibrium measurements) in the cases where  $Q$  is large. This comparison affords a valuable means of avoiding large errors in the experimental values, such, for example, as those yielded by potential



measurements with lead electrodes in sodium hydrosulphide solutions.

Sulphide.	$\frac{Q}{2 \times 23100}$	$E_K$	L, calculated from $Q$ , $E_A$ and $E_K$ .	L, observed.	Observer.
MnS	0.961	+ 1.075 <sup>2</sup>	$1.4 \times 10^{-15}$	—	—
FeS	0.471	+ 0.470 <sup>5</sup>	$1.5 \times 10^{-19}$	$3.7 \times 10^{-19}$	B. & Z.
Tl <sub>2</sub> S	0.425	+ 0.322	$(4.5 \times 10^{-23})^1$	$4.5 \times 10^{-23}$	Glaxelli <sup>7</sup>
$\beta$ ZnS <sup>3</sup>	0.888 <sup>9</sup>	+ 0.770	$1.2 \times 10^{-23}$	$ca. 5 \times 10^{-23}$	Glaxelli <sup>7</sup>
NiS	0.375	+ 0.228	$1.4 \times 10^{-24}$	—	—
CoS	0.430	+ 0.232	$3.0 \times 10^{-26}$	—	—
CdS	0.700	+ 0.420 <sup>11</sup>	$3.6 \times 10^{-29}$	$5.0 \times 10^{-29}$	B. & Z.
PbS	0.400	$\left\{ \begin{array}{l} + 0.151 \\ + 0.120^4 \end{array} \right.$	$\left\{ \begin{array}{l} 4.2 \times 10^{-28} \\ 3.6 \times 10^{-29} \end{array} \right.$	$3.4 \times 10^{-28}$	—
CuS	0.375	- 0.329	$8.5 \times 10^{-44}$	$\left\{ \begin{array}{l} 1.2 \times 10^{-12} \\ 5.9 \times 10^{-42} \\ 3.9 \times 10^{-51} \end{array} \right.$	Knox <sup>7</sup> Immerwahr <sup>8</sup> Bernfeld <sup>7</sup>
Ag <sub>2</sub> S	0.072	- 0.798 <sup>6</sup>	$1.6 \times 10^{-19}$	$\left\{ \begin{array}{l} 3.9 \times 10^{-50} \\ 4.8 \times 10^{-53} \end{array} \right.$	Knox <sup>7</sup> Lucas <sup>7</sup>
HgS	$\left\{ \begin{array}{l} 0.193^{10} \\ 0.134 \end{array} \right.$	- 0.753	$\left\{ \begin{array}{l} 2.0 \times 10^{-52} \\ 1.0 \times 10^{-49} \end{array} \right.$	$\left\{ \begin{array}{l} 1.0 \times 10^{-53} \\ 6.7 \times 10^{-48} \end{array} \right.$	Knox <sup>7</sup> Immerwahr <sup>7</sup>

<sup>1</sup> Standard used in calculating  $E_A$ .

<sup>2</sup> All the values in this column are taken from Wilsmore's table (*Zeit. phys. Chem.*, **35**, 291 (1900)), except where otherwise stated.

<sup>3</sup> The variety precipitated from alkaline solution. The observed value of L is recalculated from Glaxelli's results, as Bruner and Zawadski's value appears to contain an error.

<sup>4</sup> W. K. Lewis's value. (*Dissert.* Breslau, 1908; Abegg's *Handbuch*, 4<sup>te</sup> Gruppe, p. 638).

<sup>5</sup> Foerster, *Beiträge zur Kenntnis des elektrochemischen Verhaltens des Eisens*, 1909.

<sup>6</sup> G. N. Lewis, *Zeit. phys. Chem.*, **55**, 473 (1906). This value agrees with that found by Brislee (*Trans. Farad. Soc.*, Dec., 1908).

<sup>7</sup> *loc. cit.*

<sup>8</sup> *Zeit. für Elektrochemie*, **7**, 478 (1901).

<sup>9</sup> Berthelot, *Thermochemie*, Paris, 1897, II, 308.

<sup>10</sup> Varet (Berthelot, *Thermochemie*, II, 359).

<sup>11</sup> The electrolytic potential of cadmium was redetermined by Jaques (*Trans. Farad. Soc.*, Vol. V. Part III (1910)), and found to be +0.395  $\pm$  0.006 volt at 25°. This gives  $L = 1.55 \times 10^{-29}$ .

## APPENDIX I

### THE HYDRATE THEORY

VARIOUS circumstances have led to a widely spread belief that many electrolytes are "hydrated" in solution; that is, that each molecule of solute is present in combination with one or more molecules of water. Much experimental work has been done, and a great deal of discussion has taken place on the subject, but up to the present very little definite evidence has been obtained.

Probably the most reliable evidence for the existence of hydrates in solution has been gained by Jones and his co-workers, a *résumé* and bibliography of whose work was given by Jones (*Zeit. phys. Chem.*, **74**, 325 (1910)).

In 1894 Jones (*Zeit. phys. Chem.*, **13**, 416) determined the freezing points of mixtures of sulphuric acid and water in acetic acid as solvent. The results showed clearly that combination had occurred, and was, in fact, so nearly complete, that almost exactly one molecule of water disappeared for each molecule of sulphuric acid added, indicating the formation of the hydrate  $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$ . The values in solutions containing more water appeared to show the formation to a smaller extent of the hydrate  $\text{H}_2\text{SO}_4, 2\text{H}_2\text{O}$ . Since these hydrates are formed in acetic acid solution, we may conclude that they are also present in aqueous solutions of sulphuric acid.

Jones and Ota (*Amer. Chem. Jour.*, **22**, 5 (1899)) in the course of an investigation of the complex formation occurring in solutions of certain double salts, determined their freezing points in order to gain an insight into the molecular condition of the solute. It was found that as the concentration was increased, the molecular depression of the freezing point, instead of becoming continually less, passed through a minimum at a concentration between 0.1 and 0.2 molar, and then increased very rapidly. The same phenomenon had already been observed by

Arrhenius (*Zeit. phys. Chem.*, **2**, 496 (1888)). This fact cannot be explained by assuming any possible mode of combination of the substances in solution, since according to the law of mass-action, dissociation must increase as the solution is diluted, and the molecular depression must therefore increase also. Jones therefore sought to explain the phenomenon by assuming that the solvent entered into combination with the solute, forming, in the case of water solutions, "hydrates." If this occurs, the active mass of water in a solution will be less than that calculated from its composition, without allowing for the formation of hydrates. As the concentration increases, the proportion of the water existing in combination with the solute will become greater, so that strong solutions in which hydrates are present should behave with respect to freezing point depression as if they were a great deal stronger than they really are.

Further experimental work showed that a great many single salts show a minimum in the molecular depression, and it was found that, in general, salts which are hygroscopic or crystallise with much water of crystallisation show the highest molecular depression in strong solutions.

Later, other methods were brought to bear upon the subject. It was shown that salts which crystallised with much water gave solutions which had the highest temperature coefficients of the electrical conductivity. If we assume, as seems probable, that most hydrates are exothermic compounds, and tend to dissociate with rise in temperature, it is evident that the ionic volumes will diminish, and that the conductivity of a solution containing hydrated ions should, *ceteris paribus*, increase more rapidly with rise of temperature than that of a solution in which the ions are not hydrated. Further, the temperature coefficient increased very fast with dilution in the case of the supposedly hydrated salts, and much more slowly in the case of the unhydrated ones.

Jones has also observed the absorption spectra of many solutions of metallic salts, and claims that the results support his theory. He criticises the theory of Donnan and Bassett regarding the colour of cobalt chloride solutions, but his arguments do not appear to show the incorrectness of the theory. Jones states that the dissociation of the complex ion should increase with rise in temperature, and therefore, if the colour of the solution is affected by complex formation, the effect of

raising the temperature should be opposed to that of increasing the concentration, and spectroscopic observations do not support this conclusion. But actually it was shown (Donnan and Bassett, *loc. cit.*) that the formation of the complex ion in cobalt chloride solutions is probably endothermic, and rise of temperature should therefore have an effect upon the colour precisely similar to that of increase in concentration, in good agreement with the facts.

Walden (*Zeit. phys. Chem.*, **55**, 207 (1906)) showed that for a given electrolyte (tetraethylammonium iodide) the product of the viscosity and the maximum molecular conductivity of a solution is independent of the solvent and the temperature. About thirty solvents were examined. Walden considers that this can be accounted for by assuming that each ion carries with it some of the solvent.

Riesenfeld and Reinhold (*Zeit. phys. Chem.*, **66**, 672) point out that the ionic mobility should, *ceteris paribus*, depend upon the ionic volume, and should decrease as the ionic volume increases. In the series of metals Li, Na, K, Rb, and Cs, the atomic volume rises continuously from 12 to 71, while the ionic mobilities also increase from 33.4 to 68.2. This can be explained by assuming that the ions carry with them various quantities of water, the lithium ion being most hydrated and the caesium ion least.

Further, the temperature coefficient of the ionic mobility at infinite dilution is nearly the same for many monovalent ions, and is equal to the temperature coefficient of the fluidity of water. Thus it appears as if the friction during electrolysis exists between water and water. The same relation was observed by Walden (*loc. cit.*) in all the solvents examined by him, and is included in his law relating to viscosity and conductivity.

Another method of attacking the problem of hydration consists in measuring the depression of the solubility of a substance caused by addition of an indifferent solute to the solution. This subject is discussed by Philip (*Trans. Farad. Soc.*, Oct., 1907), from whose paper the following tables are taken.

TABLE I.

(Calculated from Knopp, *Zeit. phys. Chem.*, **48**, 97 (1904)), 20° C.

Percentage of chloral Hydrate.	Volume of Hydrogen absorbed	
	By 1 litre of solution.	By 1000 grams of water.
4.91	18.39	18.95
7.69	18.02	18.92
14.56	17.12	18.78
18.77	16.53	18.69
29.5	15.42	15.07

TABLE II.

(Calculated from Steiner, *Weid. Ann.*, **52**, 275 (1894)), 15° C.

Percentage of Cane Sugar.	Volume of Hydrogen absorbed		Molecules of water to 1 mol. Cane Sugar.
	By 1 litre of solution.	By 1000 grams of water.	
0.00	—	18.83	—
16.67	15.61	17.55	6.5
30.08	12.84	16.27	6.0
47.65	8.92	13.95	5.4

TABLE III.

(Steiner) 15°.

Percentage of KCl.	Volume of Hydrogen absorbed		Average molecular Hydration.
	By 1 litre of solution.	By 1000 grams of water.	
0.00	—	18.83	—
3.83	16.67	16.93	10.5
7.48	14.89	15.36	9.4
12.13	12.79	13.5	8.5
19.21	10.12	11.09	7.2

TABLE IV.

(Knopp) 20°.

Percentage of KCl.	Average molecular hydration.
1.09	9.8
2.12	11.1
4.07	10.0
6.37	10.0
7.38	10.0
13.61	7.6
0	

Knowing the density of the solutions, we can split the mass of any volume of the solution into grams of water and solute respectively, and thus calculate the volume of hydrogen absorbed by 1000 grams of water, assuming that the gas does not dissolve in the solute. In the case of chloral hydrate the absorption coefficient calculated in this way for the water alone remains practically constant, while for solutions of cane sugar and potassium chloride it decreases quickly. It seems very probable that this decrease is due to hydration of the solute, less free water being present in the solutions than the amount calculated from their composition. If we assume that this is the case, we can readily calculate the amount of water that must have been removed by each molecule of the solute, and thus obtain the values given in Tables II., III., and IV. Similar measurements have been made (Philip, *loc. cit.*), with many other salts, and in each case the results show a considerable degree of hydration.

The equation of van der Waals can be applied in many cases to strong solutions of non-electrolytes (Bredig, *Zeit. phys. Chem.*, 4, 44; Noyes, *ibid.*, 5, 83; Berkeley and Hartley, *Trans. Roy. Soc.*, 206, A, 481; Sackur, *Jahresbericht der Schlesischen Ges. für Vaterländische Cultur*, 86, June, 1908) by assuming suitable values for  $b$ . The values of  $b$  obtained in this way always diminish rapidly as the temperature is raised, however, and probably include the volume of a quantity of water in combination with the solute, the hydrate so formed tending to dissociate as the temperature rises.

For a discussion of the theory of hydration in solutions, the reader is referred to the Transactions of the Faraday Society, Volume III., Part 2 (1907) (a general discussion on "Hydrates in

Solution": copies can be obtained separately), also Dhar, *Zeit. für Elektrochemie*, **20**, 57 (1914).

The general result of the evidence is that it is probable that many electrolytes and some non-electrolytes exist in solution in combination with a large number of molecules of the solvent. Thus, in many dilute solutions, *instead of free ions or molecules, we are probably dealing with complex compounds of these with a number of molecules of the solvent.* In dilute solution these compounds must be regarded as of practically constant composition, and the quantity of solvent thus combined is negligible compared with the amount present in the system. In strong solutions, on the other hand, as the concentration is altered, considerable alterations may occur in the composition of the hydrates, and further, the active mass of the solvent may be much less than that calculated from the composition of the solution with respect to solvent and solute. This theory affords a probable explanation of the deviations from the law of mass action shown by many strong solutions, and appears likely to become useful in explaining some of the difficulties met with in applying the law of mass action to strong solutions, but it does not affect the results obtained in dilute solutions where the methods discussed in this volume point to the existence of comparatively stable complex ions.

## APPENDIX II

### A THEORETICAL METHOD OF EXAMINING CERTAIN SOLUTIONS

THE following method provides for the complete analysis of any solution containing complex ions of the type  $MA_n$ , where M represents an atom of a metal and A an acid radicle.

We assume that a series of potential measurements in solutions containing a fixed amount of alkali salt of the acid and various quantities of the salt of the metal M has shown that  $q$ , the number of atoms of metal in the complex ions, has the usual value, 1.  $q$  is really the average value for all the compounds present in the solution. It cannot be less than 1 for any compound, and thus if we find the average value to be 1 it follows that  $q$  must be 1 for all the compounds (undissociated salt and complex ions and salts) in the solution.

We now proceed to make a series of potential measurements in solutions containing a fixed amount of the salt of the metal, M, and variable amounts of alkali salt. In these solutions, the total concentration of the metal,  $c$ , is made up of the concentration of free metal ions, together with those of a series of compounds of the metal with the acid radicle, A, including undissociated salt and complex ions. We therefore obtain

$$c = [M'] + [MA] + [MA_2'] + [MA_3''] + \dots + [MA_n]$$

Calling the dissociation constants of the compounds  $MA$ ,  $MA_2'$ ,  $MA_3''$ ,  $\dots$ ,  $MA_n$ ,  $K_1$ ,  $K_2$ ,  $K_3 \dots K_n$ , and using  $n$  different concentrations of alkaline salt, we have

$$\begin{aligned} c &= [M']_1 \left( 1 + \frac{[A']}{K_1} + \frac{[A']^2}{K_2} + \frac{[A']^3}{K_3} + \dots + \frac{[A']^n}{K_n} \right) \\ &= [M']_2 \left( 1 + \frac{[A']_2}{K_1} + \frac{[A']_2^2}{K_2} + \frac{[A']_2^3}{K_3} + \dots + \frac{[A']_2^n}{K_n} \right) \\ &= [M']_3 \left( 1 + \frac{[A']_3}{K_1} + \frac{[A']_3^2}{K_2} + \frac{[A']_3^3}{K_3} + \dots + \frac{[A']_3^n}{K_n} \right) \\ &= [M']_n \left( 1 + \frac{[A']_n}{K_1} + \frac{[A']_n^2}{K_2} + \frac{[A']_n^3}{K_3} + \dots + \frac{[A']_n^n}{K_n} \right) \end{aligned}$$



This set of equations can be solved for  $K_1, K_2, K_3, \dots K_n$ , and we thus find the formulae, dissociation constants and concentrations of all the compounds in the solution.

Practically, the method has the disadvantage that small errors in the potential measurements become greatly magnified in the calculation. Also, the concentration of alkali salt must be large compared with the total concentration of the metal, to enable us to calculate the concentration of the ion  $A'$ , while on the other hand the concentrations of the different solutions used must differ widely from one another. The method has never been applied successfully to a set of experimental results, but it is nevertheless useful in enabling us to form a conception of the state of affairs in a solution containing more than one complex ion.

We have worked out the expressions for a monovalent metal, but obviously those for a di- or trivalent one would be precisely the same, the first two or three constants corresponding to the undissociated salt and its different stages of dissociation.

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